

**Chino Mines Company
Hurley, New Mexico**

**Administrative Order on Consent
Interim Removal Action Work Plan
Smelter/Tailing Soil Investigation Units**

November 2007

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Our Ref.:
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Date:
November 2007

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Executive Summary

ARCADIS US, Inc. (ARCADIS BBL) has prepared this Interim Removal Action Work Plan (IRAWP) for Chino Mines Company (Chino) to address copper impacts to the north, and west of Hurley from historic mill and smelter operations. This Excavation IRAWP considers the results of the Remedial Investigation (RI) and previous investigations to propose alternatives and recommendations for interim remedial action for surface soils in the Smelter and Tailings Soils Investigation Unit (STSIU).

The STSIU is located primarily within the San Vicente Basin, a broad lowland area characterized by several dry washes and gullies with sandy bottoms. Areas west and north of the smelter and tailing facilities are relatively flat at an approximate elevation of 5,700 feet above mean sea level (msl), while increasing topographic relief is observed to the northeast and east, rising to an elevation of approximately 6,400 feet above msl. Soils are generally rocky and thin with little organic material.

This IRAWP considers information and data gathered as part of previous investigations, including:

- Background Report (Chino, 1995)
- Phase II Ecological Remedial Investigation (ARCADIS JSA, 2001)
- Smelter/Tailing Soils Investigation Unit Remedial Investigation (December 2006) (SRK, 2006)

While the human health risk assessment has not yet been submitted, based on algorithms and parameters presented in Gradient (2005) and all data including SRK (2006), Chino estimated copper to drive potential human health risk. The Final Site-Wide Ecological Risk Assessment (ERA) also concluded that copper was the driver constituent for small ground feeding birds, the most sensitive receptor, exposed to soil (Newfields, 2005). This STSIU Interim Removal Action Work Plan will use the remedial criteria of 5,000 mg/kg as established for the Hurley Soils Investigation Unit (IU), for upland surface soil (0 to 1 inch depth) to be protective of human health.

Approximately 190 acres has been delineated for excavation to a depth of 6 inches below existing grade, based on existing copper soil data. It is assumed that the impacts are depositional in nature and therefore the majority of impacts will occur in the shallow soil. Excavation depths presented in this IRAWP are assumed to represent a conservative approach that will capture the impacted soil associated with air dispersion of copper minerals coupled with a small amount of vertical migration due to leaching with rain water.

Final contouring of the excavation areas will be accomplished through field fitting to existing contours at the perimeter of the work areas. The excavation areas will be final graded to promote positive drainage and minimize erosion. Best Management Practices (BMPs) will be utilized to limit erosion and sedimentation within the work area. BMPs and monitoring will also be utilized to limit dust generation and monitor for dust levels at the project perimeter for protection of worker and residential health.

Approximately 384 confirmation samples will be collected using X-Ray Florescence following excavation. Ten percent of the samples collected will be sent for offsite laboratory confirmation per EPA Method 200.7 and soil paste pH per American Society of Agronomy Method (ASA) Monograph 9.

Restoration will be completed in the excavation areas specified to the west and north of Hurley. Reseeding and restoration will be implemented utilizing the Closure Closeout Plan as guidance for the seed mix and application rate. Vegetation BMP inspections will be conducted following restoration of the disturbed areas.

The Interim Removal Action Completion Report will be prepared and submitted for the New Mexico Environment Department (NMED) review and approval within 90 days of completion of field activities.

1.0 Introduction

1.1 Purpose

This Interim Removal Action Work Plan (IRAWP) for the Smelter and Tailing Soils Investigation Unit (STSIU) has been prepared for Chino Mines Company (Chino) to present an excavation interim action measure for addressing surface soil impacts in the Smelter and Tailing Soils Investigation Unit at the Chino site (Site) located in Hurley, New Mexico (Figure 1). The Administrative Order on Consent (AOC) between Chino and the NMED recognized that historical mining, milling and leaching practices conducted by Chino and others may have affected the local environment (NMED, 1994). To address the AOC, multiple investigations have been conducted at the Site to characterize the nature and extent of impacts related to historic mining operations, including impacts to the STSIU. The *Administrative Order on Consent Remedial Investigation Report Smelter/Tailing Soils Investigation Unit* (RI) consists of an evaluation of surface soil and other potentially affected media in the STSIU (SRK, 2006). This IRAWP considers the results of the RI and previous investigations to propose alternatives and recommendations for interim remedial action for surface soils in the STSIU.

1.2 Site Description

This section describes the Site, and focuses on the STSIU where appropriate. Site setting, physical features, geology and climate are discussed below.

The Site was described in detail in the *Remedial Investigation Background Report - Chino Mine Investigation Area* (Chino, 1995). This site description was updated for the STSIU in the RI (SRK, 2006). The following description of the Site is mainly adapted from these sources, in particular the RI.

Multiple investigation units (IUs) associated with mining and smelting operations at the Site were designated in Appendix A of the AOC. These included the Lampbright IU, Hanover Creek Channel IU, Whitewater Creek Channel IU, Smelter IU, Hurley Soil IU, and the Tailing Soils IU. The Hanover and Whitewater Creek Channel IUs have since been combined to form the Hanover/Whitewater Creek IU. The Smelter and Tailing Soils IUs have also been combined to form the STSIU. Figure 1 presents a Site Location map.

This IRAWP specifically addresses surface soil impacts in the STSIU. The STSIU includes the copper smelter, ancillary facilities including the former Hurley Concentrator, and the tailing disposal facilities. The AOC defines the tailing area as all soils adjacent to the Chino tailing pond facility and those soils shown to be potentially affected by the tailing.

The Hurley Smelter, located in Hurley, New Mexico, is bounded by the Town of Hurley to the west, Whitewater Creek to the northeast, Lake One to the east and the tailing impoundments to the south. Current land uses adjacent to the smelter are residential in the towns of Hurley and North Hurley, tailing disposal south of the smelter, and livestock grazing elsewhere. Chino owns the majority of the land within the STSIU, with the exception of private residential areas. The majority of Chino-owned land located west of Highway 180 and east of Whitewater Creek is currently leased for livestock grazing.

Chino maintains 24-hour, 7 days a week security within the smelter operational area. Motor vehicle access to the operational area is controlled via locked service entrances or manned security gates. Perimeter fencing around the smelter operational area inhibits pedestrian access. Further, Chino security routinely patrols the former Smelter IU area to the east of Whitewater Creek to prevent unauthorized access.

The STSIU is located primarily within the San Vicente Basin, a broad lowland area characterized by several dry washes and gullies with sandy bottoms. Areas west and north of the smelter and tailing facilities are relatively flat at an approximate elevation of 5,700 feet above mean sea level (msl), while increasing topographic relief is observed to the northeast and east, rising to an elevation of approximately 6,400 feet above msl. Soils are generally rocky and thin with little organic material.

The Site is located within a complex geologic region that constitutes a transition zone between the Colorado Plateau to the north and the Basin and Range structures to the south. This transition zone is a northwest-trending structural belt, 50 to 75 miles wide, and is characterized by features related to Late Cretaceous and Miocene intrusive activity. The primary surficial geologic units in the STSIU are rhyolite, Gila Conglomerate and alluvial deposits. The rhyolite consists of welded tuff. The Gila Conglomerate consists predominantly of poorly sorted, unconsolidated to highly consolidated sand, gravel and silty gravel, deposited as coalescing alluvial fans. Alluvial deposits, associated with drainages and stream channels, are similar to the Gila Conglomerate in composition. The most predominant alluvial deposits in the vicinity of the STSIU are sediments from Whitewater Creek.

Whitewater Creek runs along the eastern side of the Hurley Smelter and tailing ponds. Field observations indicate that surface water flow in Whitewater Creek occurs ephemerally after significant rainfall events. Runoff events in the upper reaches of Whitewater Creek typically infiltrate into the streambed before reaching the STSIU.

The property is located in a semi-arid region of southwestern New Mexico. The site has a low relative humidity and exhibits a wide range in daily and annual temperatures. Average monthly temperature measurements, recorded at the Fort Bayard weather station (north of Hurley), range from a low of 38.4°F in January to a high of 72.5°F in July. The average annual temperature is 55.1°F. The average annual precipitation is 15.4 inches per year with most of the rainfall occurring during July, August and September as brief, but occasionally high intensity, thunderstorms. The prevailing wind direction is from the west-northwest with an average wind speed of approximately eight miles per hour.

1.3 Report Organization

The remaining sections of this report are organized as follows:

- Section 2 presents a description of Previous Investigations;
- Section 3 details the Interim Action;
- Section 4 describes the review of applicable regulations and permits; and
- Section 5 provides document references.

2.0 Previous Investigations

This section presents information regarding historic operations of the STSIU and the nature and extent of surface soil impacts in the STSIU. Historic operations are described for the Smelter and the Tailing IUs. Three previous reports contain detailed information related to STSIU field investigations; the Background Report (Chino, 1995), the Ecological Remedial Investigation (ARCADIS JSA, 2001) and the STSIU RI (SRK, 2006). Results of these three investigations pertaining to upland soils are presented below. Surface soil copper concentrations are presented on Figure 2.

2.1 Smelter Investigation Unit Description

As described in the AOC, the Smelter IU included the smelter facility and surrounding areas, but excluded the Hurley Soils IU and the Tailing Soils IU (NMED, 1994). The original investigation area for the Smelter IU extended approximately 5.5 miles to the east of the smelter and approximately 1.5 miles to the west of the smelter, with a limited area to the north of the smelter (Figure 1) (Chino, 1995). Historic sources in the Smelter IU are smelter emissions and historic material handling operations.

Historic smelter emissions consist of stack emissions and historic fugitive gas/dust emissions from smelting and refining of copper-bearing materials. Historic stack emissions began with the start of smelting activity in 1939. The stack functions as a vent for off-gases from furnace and converter operations. Following promulgation of state and federal air quality permit programs in the 1970s, Chino implemented pollution controls within the smelter facility to meet regulatory requirements. Metal emissions from the stack were presumably greater prior to implementation of these controls.

Historic material handling operations included ore handling and concentrate handling. Ore handling included the transport of ore from the Santa Rita Mining District by open-top rail cars. Rail cars passed through Hurley and entered the smelter facility west of the smelter, destined for the ore reduction facility adjacent to the Hurley Concentrator. The ore was subjected to crushing and grinding within the ore reduction facility prior to concentrating of the ore. The average copper ore grade from the Santa Rita mining district was 0.88% from 1952 through 1980. Chino concentrate leaving the Hurley Concentrator averaged between 20-25% copper.

Concentrate handling included stockpiling and transfer of copper concentrate from the Hurley Concentrator until 1982 and precipitation plant. Locations of historic concentrate/precipitate handling areas include the Hurley Concentrator, temporary concentrate stockpile area, temporary precipitate stockpile area, and underground concentrate storage bins.

2.2 Tailing Soils Investigation Unit Description

As described in the AOC, the Tailing Area Soils Investigation Unit included soils surrounding the Chino tailing impoundments or ponds southwest of Hurley that have potentially been impacted by operations at the tailing ponds (NMED, 1994). These impoundments and ancillary support facilities for water storage and recycling (e.g., Axiflo Lake) are the primary facilities operated by Chino within the Tailing portion of the STSIU (Figure 1).

The source of primary interest for the Tailing Soils IU is the tailing material, as well as the soil impacted by movement of tailing material from the permitted tailing ponds to the soils around it. Movement occurred primarily through wind erosion of material from the tailing impoundments and subsequent deposition. This release mechanism is both historic and potentially active. Two other release mechanisms, storm water erosion

and tailing discharge beyond the pond perimeter, may have also released materials from the tailing to the surrounding soils.

Tailing have been generated at two facilities: the Hurley Concentrator and the Ivanhoe Concentrator. Tailing are pumped to the tailing ponds through a pipeline and deposited into a pond. Tailing decant water is subsequently pumped to Axiflo Lake for reuse and recycling. Constituents added to the tailing process include surfactant and lime. Surfactant is added to aid frothing and lime is added to separate pyrite from other surface ore minerals during flotation. Lime is added at approximately 12 pounds or more per ton of ore. The pH of the tailing slurry is generally above 11 due to the addition of lime, and the pH of decant from the ponds was usually greater than 7. Historically, acid plant effluent from the Hurley Smelter was also mixed with the tailing slurry before deposition of the mixture into the tailing ponds.

The coarser- and finer-fractions in whole tailing are typically described as sands and slimes, respectively. The sand component represents material that is coarser than a Number 200 sieve that has openings of 0.075 mm. The slimes fraction is finer than these openings and composed of silt- and clay-sized particles. Tailing particles characterized in terms of the Unified Soil Classification System (USCS) generally range from silty-sand (SM) to low-plasticity silt (SL). Average sand, silt and clay content currently ranges from 35 to 62 percent, 35 to 52 percent and 5 to 20 percent, respectively. The mineralogical composition of tailing is primarily quartz, plagioclase, potassium feldspar, muscovite, chlorite/clays and pyrite. Other minerals identified in tailing are magnetite, dolomite, calcite and garnet, which are associated with the mining of calcitic sedimentary rocks.

2.3 Background Investigation

The Smelter IU and Tailing Areas Soils IU were subject to separate field investigations in 1995, which were summarized in the Background Report (Chino, 1995). For upland areas, the primary contaminant sources and release mechanisms are the smelter emissions and windblown tailing. Prevailing winds tend to be southeasterly at the smelter operational area (Chino, 1995). Therefore, soil in the areas to the south and east of the smelter and the tailing impoundment are likely to be most affected by dryfall from these aerial sources.

The objective of the Background investigation for the Smelter IU was to preliminarily assess whether historic operations at the smelter resulted in a potential release of smelter-related constituents to surrounding environmental media. The objective of the background investigation for the Tailing Area Soils IU was to characterize tailing-impacted soils based on existing data and limited data collection. The results and recommendations from these investigations are summarized below.

2.3.1 Smelter Investigation Unit

Sampling was conducting in May 1995 to characterize surface soils surrounding the smelter facility. Samples were collected up to a distance 5.5 miles to the east of the smelter and 1.5 miles west of the smelter. The Background Investigation emphasized areas to the east of the smelter due to the prevailing westerly and northwesterly winds. Sample locations were chosen based on a 0.5-mile grid, increasing to a 1-mile grid at a distance of 1.5 miles from the smelter. The following samples were collected:

- nineteen surface soil (0 to 1 inch depth) samples to the east of the smelter;
- nine surface soil samples to the west of the smelter;
- two deep soil (3 to 6 inch depth) samples, one to the east and one to the west, within 1.5 miles of the smelter;
- two surface soil samples co-located with the deep soil samples; and

- two surface soil samples to the north of the smelter.

Samples were analyzed for the 11 metals found in historic smelter emissions (see Section 2.1), sulfate and pH. The smelter investigation indicated the following soil sample results:

- Antimony, arsenic, barium, chromium and silver concentrations in surface soil were comparable to concentrations in reference area soils not impacted by site operation. Mercury and selenium were not detected, however the selenium detection limit was elevated above reference sample concentrations.
- Surface soils to the west and east of the smelter exhibited elevated concentrations of copper, molybdenum, cadmium and lead. Maximum concentrations of select constituents in surface soil, 0 to 1 inch below ground surface (bgs), were 5,240 mg/kg of copper, 75.9 mg/kg of molybdenum, 29.1 mg/kg of cadmium, and 143 mg/kg of lead.
- Soil samples collected from 3 to 6 inches below ground surface (bgs) exhibited constituent concentrations that were approximately 2 to 20 times less than the corresponding analyte concentrations in surface soil. The vertical distribution of constituents in soil was consistent with a pattern of historic deposition of airborne particulates.
- Constituent concentrations decreased with increasing distance from the smelter.

The RI Background Report (Chino, 1995) recognized that additional sampling would be required as part of the RI. The report recommended collection of soil samples to fully define the nature and extent of impact.

2.3.2 Tailing Area Soils Investigation Unit

Soil samples were collected during a limited field data collection investigation conducted in May and June 1995 to characterize surface soils in the vicinity of the Tailing ponds. Soil samples were collected from areas that may have been affected by tailing migration and from reference areas that were not affected by tailing or other known industrial operations. All samples were analyzed for copper and iron, and selected samples were analyzed for additional target analytes.

The tailing soils investigation indicated the following results:

- Maximum concentrations of select constituents of interest in surface soil (0 to 1 inch below ground surface [bgs]) were 1,330 mg/kg of copper, 34.2 mg/kg of molybdenum, 1.15 mg/kg of selenium, and 24.1 mg/kg of cobalt.
- Subsurface soil samples (1 to 6 inches bgs) exhibited constituent concentrations that were approximately 1 to 5 times less than the corresponding analyte concentrations in surface soil. The vertical distribution of constituents in soil is consistent with a pattern of historic deposition of airborne particulates.
- Constituent concentrations decreased with increasing distance from the tailing ponds.

Antimony, arsenic, barium and chromium concentrations in surface soil were comparable to reference soil sample concentrations. Mercury and silver were not detected in the tailing ponds area soil samples.

The RI Background Report recognized that additional sampling would be required as a part of the RI. The RI Background Report stated that the current AOC boundary east of the tailing impoundments did not define the extent of affected soil as a consequence of tailing migration.

2.4 Ecological IU Remedial Investigation (RI)

A Phase II Ecological RI was conducted to address potential ecological risk associated with former and current operations at the site (ARCADIS JSA, 2001). The Ecological IU encompasses all the IUs designated by the AOC and is characterized by complex geology, topography, variable climate, and ecology. Because of the landscape scale and complexity of the Ecological IU, the conceptual site model (CSM) was separated into two distinct components for discussion purposes: (1) the upland, and (2) the ephemeral drainage. The upland portion of the Ecological IU (Upland Investigation Area, Upland IA) corresponds to the area of interest for this proposed STSIU Interim Action. The Upland IA is approximately 10 to 12 square miles south-southeast of the town of Hurley and includes the Smelter and Tailing Soils IUs.

Fifteen sampling locations were selected to represent the Upland IA and six sampling locations were selected to represent Upland IA reference conditions. Soil samples were collected from the 0 to 6 inch depth interval at all sampling locations. Soil samples were collected from deeper intervals (e.g., 6–12 inch depth interval) at select locations depending upon soil horizons encountered at each sampling location. Concentration of constituents of concern (COC) in Upland IA soils were compared with concentrations of COC in Upland IA reference samples using statistical techniques. The primary results from this investigation include the following:

- arsenic, barium, boron, iron, and manganese were within the reference range at all locations;
- aluminum, calcium, chromium, lead, mercury, thallium, and zinc were above the reference range at a limited number (<4) of select locations;
- cobalt, molybdenum, and nickel were each above the reference range at five locations that were consistent with a concentration gradient;
- cadmium and selenium were elevated at most locations. Cadmium concentrations in reference location soil ranged from 0.44 to 0.66 mg/kg while cadmium concentrations in site soil (0–6 inch interval) ranged from 0.52 to 3.80 mg/kg. Selenium concentrations in reference location soil ranged from 0.10 to 0.25 mg/kg while selenium concentrations in site soil (0–6 inch interval) ranged from 0.3 to 1.9 mg/kg;
- copper was elevated at all locations. Copper concentrations in reference location soil ranged from 39 to 75 mg/kg while copper concentrations in site soil (0–6 inch interval) ranged from 109 to 3,517 mg/kg. The most elevated concentrations of copper were measured in samples collected nearest to the smelter and tailing areas; and
- based on statistical testing and surface/subsurface soil concentration ratios, subsurface soils have likely not been affected by historical mineral processing.

Based on Interval and Equivalence results, cadmium, copper, and selenium were potentially elevated in Ecological IU Upland IA site surface soil relative to the selected reference locations.

2.5 STSIU Remedial Investigation (RI)

This section describes the findings of the AOC RI - STSIU (SRK, 2006). The field investigation occurred during October and November 2004. A supplemental field investigation followed during July and August 2006. Soil samples collected from the RI included undisturbed surface soil (0 to 1 inch bgs), disturbed surface soil (0 to 1 inch bgs), and undisturbed shallow soils (0 to 6 inches bgs). Sixty-one undisturbed surface soil samples were collected to support the human health risk assessment. Supplemental surface soil samples were collected in two disturbed areas; 5 samples from the smelter area and 8 samples from alongside the railroad track north of Hurley. Additional sampling was also conducted to supplement the ecological risk assessment to characterize undisturbed shallow soil west of the tailing impoundments (8 samples) and east of the tailing impoundments (17 samples). For all samples, particle size analysis was performed using US Standard Sieve sizes #10 (2 millimeters) and #60 (0.25 millimeters). Only the portion that passed through the #60 mesh was analyzed for metals, including arsenic, barium, cadmium, cobalt, copper, lead, manganese, molybdenum, selenium, silver, and zinc.

Results for copper from the soil investigations included the following (Figure 2):

- concentrations of copper in reference soil ranged from 43 to 207 mg/kg;
- concentrations of copper in 61 undisturbed surface soil (0 – 6 inch) samples collected from east and west of the smelter operational area ranged from 272 to 12,100 mg/kg;
- concentrations of copper in 5 disturbed surface soil (0 – 6 inch) samples collected within the western fence boundary of the smelter area ranged from 10,500 to 30,500 mg/kg;
- concentrations of copper in 8 disturbed surface soil (0 – 6”) samples collected along the railroad tracks between the towns of Hurley and Bayard ranged from 660 to 5,350 mg/kg;
- concentrations of copper in 8 undisturbed shallow soil (0 – 6”) samples collected west of the tailing area ranged from 157 to 1,290 mg/kg; and
- concentrations of copper in 17 undisturbed shallow soil (0 – 6”) samples collected east of the tailing area ranged from 237 to 1,400 mg/kg.

2.6 Supplemental Data Gathering

Golder Inc. conducted a supplemental data gathering event in October 2007 to define for final remediation purposes the lateral extent of soil impacts at or greater than 5,000 ppm copper. This information is for use in the contractor bid process. An additional 274 soil samples were collected and analyzed using XRF technology for total copper concentration. Figure 2 represents the data collected to date within the areas proposed for excavation.

2.7 Golf Course Pilot Study

SRK performed a pilot study in 2005 to determine an effective and efficient method to lower average concentrations of copper in soil to below 5,000 mg/kg in a select area of the golf course. Copper concentration data collected as part of this pilot study are included on Figure 2. These data were utilized for delineation of copper impacts on the west side of the stacks.

2.8 Human and Ecological Health Risk

Due to multiple sources and stressors, system heterogeneity, and a variety of transport and release mechanisms, the STSIU Interim Action area is a complex physical system that affects metals distribution and transport, plant and wildlife exposure scenarios, and the inherent variability in the plant and wildlife populations and

communities that exist at the site. Site-specific data have been evaluated to ascertain potential risk to human and ecological health. Results of these evaluations with respect to upland soil in the STSIU are provided in the following sections.

2.8.1 Human Health

A human health risk assessment (HHRA) for the STSIU is being developed by the NMED risk assessor. Surface soil within the STSIU has been impacted with COCs from former smelter emissions and wind-blown dust from the tailing ponds. Thus, based on the human health risk assessment work plan, there is potential for direct human exposure to COCs in surface soils via incidental soils ingestion, foodstuffs, dermal contact, and inhalation for current and future residents, construction workers, industrial workers, ranchers, recreators, and trespassers (Gradient, 2005).

2.8.2 Ecological Risk

Two ecological risk assessments (ERAs) have been completed for the STSIU: the final Site-Wide ERA Report (Newfields, 2006) and the draft ERA for the STSIU (Newfields, 2007). Both documents present similar findings of risk which indicate that risk of toxicity to plants and wildlife from soil is primarily due to elevated copper concentrations and depressed pH which is consistent with the proposed IRA. The final Site-Wide ERA (Newfields, 2006) included a screening-level ERA that was used to identify constituents of potential concern (COPCs), the receptors that may be exposed to the COPCs, and the exposure pathways to be assessed in the ERA. ERA assessment endpoints for upland receptors included upland vegetation communities and avian and mammalian wildlife. Results of a conservative secondary wildlife exposure screen (SWES) identified small ground-feeding birds as the only terrestrial receptor with a potential for unacceptable risk due to ingestion of copper (Newfields, 2005). Based on an assessment using conservative bioavailability levels and no observed adverse effects level (NOAEL) toxicity reference values (TRVs), results indicated that potential acceptable risk levels were exceeded at a number of locations at the site. The ERA for STSIU (Newfields, 2007) further caveated these findings by indicating that potentially significant toxicity to the terrestrial plant community and terrestrial wildlife (small ground-feeding birds) is predicted within a half to one mile of the smelter and tailings impoundments.

2.8.3 Rangeland Condition

Rangeland condition is affected by a number of factors including soil type, pH, elevation, and aspect; precipitation and vegetation pattern formation; human use, grazing, and fire patterns; and plant and wildlife adaptation as an effect of soil mineralization and mining impacts. Detailed descriptions of these factors for the STSIU are presented in the Ecological IU Remedial Investigation Report (ARCADIS JSA, 2001). Phytotoxic effects from copper could occur at the site due to elevated copper concentrations and depressed pH in site soil. The potential for direct phytotoxic effects, cascading adverse effects, and secondary stressors resulting from habitat loss, are of concern. Potential adverse effects could include increased erosion; nutrient runoff; penetration of pests, weeds, and other exotic species; and altered hydrologic regimes. Although impacts from mining activities may have affected rangeland conditions in the STSIU, the interaction of other environmental and anthropogenic stressors, such as climate and grazing, is complex. All stressors were preliminarily characterized in 1997 as part of a rangeland condition study conducted by Chino under the Phase I Ecological IU RI Proposal (Woodward-Clyde, 1997).

The Phase I Ecological IU RI Proposal cited standard federal land management agency procedures for classification of rangeland according to ecological condition (Woodward-Clyde, 1997). Rangeland condition, or ecological status, is measured as the degree to which the vegetation of a site is different from the potential natural community characteristics of that or similar sites. Rangeland ecological condition was evaluated based on three major ecological attribute categories: (1) degree of soil stability, (2) integrity of nutrient cycle, and (3) presence of functioning recovery mechanisms. These attributes as measured by soil condition, plant composition, and plant cover, were the principal attributes used to rank and classify landscape unit (i.e., polygons) ecological conditions for the STSIU into an observed apparent trend (OAT). In addition, preliminary rangeland condition categories: excellent, good, good-fair, fair, fair-poor, and poor were also recorded. These preliminary rangeland conditions for the STSIU are presented on Figure 3. As shown on Figure 3, rangeland conditions in the STSIU range from poor to excellent.

Risk to vegetation, due to mining impacts and other stressors, was assessed during the ERA (Newfields, 2006). One primary objective of the vegetation risk analysis was to account for the potentially large range of bioavailability of metals, particularly copper, in estimating risk of phytotoxicity. Bioavailability may vary between sites but is generally affected by soil pH, organic carbon content, texture, and mineral form (Newfields, 2006). To help estimate the bioavailable fraction of metals from soil to plants, soil samples were analyzed for cupric ion activity (pCu^{2+}).

Based on the conclusions set forth in the final Site-Wide ERA, elevated concentrations of copper and other metals, combined with depressed soil pH, may have led to risk of phytotoxicity for some areas of the Chino Mine site. However, these effects were somewhat difficult to distinguish from other stressors such as climate or grazing. Adverse effects on vegetation were apparent for ERA sampling locations nearest the smelter and tailing impoundments; however, effects were highly dependent on soil pH. For example, some locations have elevated copper concentrations in soil, but have relatively high pH (>6 s.u.) and exhibit little or no evidence of phytotoxicity (Newfields, 2006). In more outlying areas, effects on vegetation were less evident, probably due, in part, to reduced contaminant loading with distance from the sources. The draft ERA for the STSIU (Newfields, 2007) further concluded that cupric ion in more outlying area soils corresponds to levels that are likely toxic to laboratory test species, not native plant species, and thus it is unclear whether there has been a significant, adverse effect on wildlife habitat quality since even under pristine conditions, vegetation cover and quality is highly variable. The draft ERA for STSIU further concluded that at Chino, the ability to quantify differences in habitat quality based on field measures is further confounded by the effects of (past) intensive grazing and other anthropogenic uses. These conclusions appear to support the idea that rangeland condition is not necessarily consistent with cupric ion concentrations, i.e., areas of low cupric ion may still be observed as having fair or good rangeland condition.

2.9 Constituents of Concern (COC)

Based on the Smelter/Tailing Soils RI Report (SRK 2006), there are several metals such as arsenic, cadmium, copper, iron and vanadium that exceed U.S. EPA Region 6 Preliminary Remediation Goals (PRGs) (Table 4-2 in the RI). Arsenic data are largely within the range of background but detects in excess of background co-occur with elevated copper (specifically along the western fence line of the smelter operational area which is not addressed by this interim action but will be addressed by closure/closeout activities). For cadmium, there was one exceedance (S53) which was co-incident with elevated copper (on the east side of the smelter). For iron, the PRG shown in the RI has been updated by EPA recently from 23,464 to 55,000 mg/kg and, therefore, there are fewer detects exceeding the PRG than shown in the RI and they are coincident with elevated copper except at five locations east of Tailing Pond 7. For vanadium, elevated detects do not co-occur with elevated copper concentrations (detected in Martin, Rustler and Lampbright Canyons) and, therefore, given that vanadium is not a key constituent in either smelter emissions or crushing operations, vanadium is not sourced by historic mineral processing. Therefore, while the human health risk assessment has not yet been submitted, based on the RI data

compared to EPA Region 6 PRGs, copper will be used to delineate the remedial area for this interim action. In addition, ecological receptors are more sensitive to copper and other metals than humans and copper was also identified as the driver constituent for small ground feeding birds, the most sensitive receptor, exposed to soil based on the conclusions presented in the final Site-Wide ERA (Newfields, 2006), and the draft ERA for STSIU (Newfields, 2007) which support the use of copper as the driver constituent for the proposed IRA.

2.10 Extent of Contamination

Based on surface soil copper concentration data for this proposed IRA, the area of upland soil with surface soil copper concentrations greater than 5,000 mg/kg and a pH above 6 is approximately 135 acres north of Hurley and 55 acres west of Hurley (190 acres total) (Figure 2). An additional area with copper concentrations exceeding 5,000 mg/kg is located to the east of the stacks: Razorback Ridge. Historical impacts at Razorback Ridge are excluded from this work plan and will be managed under a separate removal action work plan, to be submitted under separate cover.

3.0 Interim Action

3.1 Remedial Action Objectives

As discussed above, copper has been identified as the driver constituent for this interim action. Based on the Advisory Group Formal Dispute Resolution for the Chino AOC, Hurley Soils Investigation Unit (HSIU), an amendment to the AOC dated July 28, 2005 set a pre-feasibility (FS) study remedial action criterion (RAC) for the Hurley Soils Investigation Unit (HSIU) of 5,000 mg/kg for copper in soil to be protective of human health (Phelps Dodge Corporation, 2005). The source point for the copper is predominantly the old Hurley Mill as it was for the HSIU IRA which was completed in July, 2007. This STSIU Interim Action Work Plan, by using the RAC of 5,000 mg/kg for upland surface soil (0 to 1 inch depth), will be protective of human health as a continuation of the Hurley Soils IU IRA. The 5,000 mg/kg copper level should be conservative for this area because, unlike the Town of Hurley, the area is not currently used for residential purposes.

The objective of this excavation IRAWP is to remove areas where soil copper concentrations are greater than 5,000 parts per million (ppm), which is the cleanup level specified in the HSIU RAC. To be conservative and to further address potential ecological risk, the excavation is intended to also remove soil concentrations vertically down to 2,700 ppm copper. Based on this information, horizontal removal limits are defined by the 5,000 ppm copper concentration contour; whereas, the vertical delineation is defined by a copper concentration of 2,700 ppm. Since the HHRA and ERA for STSIU are not yet finalized and pre-FS RAC have not been set for the STSIU, the NMED may require a more stringent cleanup level based on ecological risk in the future.

3.2 Removal Methodology

The removal areas are shown on Figure 3. The areas include North and West of Hurley. Each area is shown in detail on Figures 4 and 5, respectively. Removal areas will be cleared for utilities through the Chino Blue Stake permit process, at least one week prior to excavation activities.

3.2.1 Removal Areas

Excavation depths are based on estimated depths of impacts. It is assumed that the impacts are depositional in nature and therefore the majority of impacts will occur in the shallow soil from ground surface to 2-inches below ground surface (bgs). Excavation depths presented in this IRAWP are assumed to represent a conservative approach that will capture the impacts associated with air dispersion of copper coupled with minor vertical migration due to leaching with rain water. Excavation depth has been defined as a minimum of 2-inches bgs, with a removal target goal of 2,700 ppm copper. For the purposes of volume estimation, and based on potential equipment limitations, 6-inches of excavation is assumed for the North and the West removal areas. This depth should account for any need to over-excavate following confirmation sampling (see Section 3.4, below).

Excavation areas depicted on Figures 4 and 5 may need to be adjusted in the field to account for existing structures and highway and railroad right-of-ways (ROW). For the purposes of these figures, and the area and volume calculations shown below, it is assumed that excavation areas are limited to within 50 feet of the rail road tracks. Excavation along side-streets will be coordinated with the local government and completed up to the existing road-side drainage ditch. Chino will plan remediation in the Highway 180 ROW areas if approval is

received from the NM Department of Transportation (DOT) under which a highway expansion project has begun.

Each of the areas will be excavated to a depth of 6 inches. In the area north of Hurley the assumed depth of top of caliche is 6 to 12 inches below ground. Soil removal will cease when caliche is encountered shallower than 6-inches bgs. Approximate excavation volumes are summarized in the following table.

TABLE 1
REMOVAL AREA DETAILS

Location (with Respect to Hurley)	Area (acres)	Depth of Excavation (inches)	Volume (CY)
West	55	6	44,400
North	135	6	108,900
Total	190		153,300

3.2.2 Site Preparation

Clearing and grubbing will be necessary prior to excavation to remove larger mesquite, and other physical obstacles such as boulders, from the work area. Cleared materials (boulders and mesquite) will be stockpiled along the perimeters of the work areas. Each debris stockpile will not exceed 1,000 cubic feet. Stockpile locations will be determined in the field and documented in the Completion Report (see Section 3.6 for details on construction documentation). Boulder and brush piles will remain at the perimeter of the construction site as these are not considered waste materials. The piles may ultimately provide some level of habitat for birds and small mammals in the area.

3.2.3 Excavation and Materials Management

Soil removal will be accomplished via soil scraping with heavy equipment. Soil removed during this excavation IRAWP will be hauled to Tailing Pond 1. Soil to be hauled to Tailing Pond 1 will be sampled and analyzed by an offsite laboratory for toxic characteristic leaching procedure (TCLP) in accordance with Resource Conservation and Recovery Act (RCRA) regulations. TCLP sampling will be targeted for excavation areas with higher concentrations based on existing field and laboratory data. The laboratory will analyze the samples for total RCRA metals as well as TCLP for the same analyte list. If the areas with higher total RCRA metals concentrations pass TCLP, it is assumed that other areas slated for excavation would also pass TCLP without analytical analyses; therefore this material would be appropriate for final disposition at Tailing Pond 1. Total analyses required will be determined based on anticipated production rates and sequencing of excavation activities.

Excavation in and near drainage features will be done so as to minimize impacts and changes to the drainage feature. Stockpiled boulders may be used following excavation as rock channel protection to limit erosion within the excavation drainage feature. Type and amount, if any, of rock used within the drainage feature will be determined based on the slope of the channel following excavation as specified by the field engineer.

Final contouring of the excavation areas will be accomplished through field fitting to existing contours at the perimeter of the work areas. The excavation areas will be final graded to promote positive drainage (i.e., no

sinks or low points). Since the excavation depths are very shallow – less than 2 feet – proposed final contours are not presented in this IRAWP. Final contours will be field fit and documented during the next scheduled aerial flight of the smelter area. Backfill is not anticipated to be necessary to complete final grades at the removal areas. Final use and restoration of the excavated areas is described in more detail in Section 3.5, below.

With the exception of sampling wastes, waste materials are not expected to be generated during this proposed IRA. Removed soil will be hauled to Tailing Pond 1; brush, trees, boulders, and rocks will be stockpiled at the perimeter of the construction site as means of final disposition. Investigation-derived-waste generated during confirmation sampling will be managed in accordance with Chino Standard Operating Procedures (SOPs).

3.3 Best Management Practices

Best Management Practices (BMPs) include those measures taken to limit sedimentation and erosion within the work areas, as well as measures taken to reduce dust emissions to both site workers and nearby residents. Preliminary BMPs selected for this project are described in the following sections. Specific BMP types and final locations will be determined in the field by the Site stormwater pollution prevention manager.

3.3.1 Sediment and Erosion Control

BMP's are employed during soil disturbance activities to limit erosion and sedimentation within and from the project area. Conceptually, silt fences, or equivalent protective BMP, will be installed at the downgradient perimeter of the excavated areas, as shown on Figure 6. In areas where the work area crosses or includes an existing drainage feature, straw bales, rocks, or sand bags will be placed across the drainage feature to limit sedimentation during storm events. Fiber rolls or silt fences will be placed following excavation within the work areas to reduce sheet flow velocity. Silt fences will not extend across drainage features. The preliminary locations of straw bale placement are also shown on Figure 6.

Additionally, one or more water trucks will be utilized, as necessary during excavation and soil movement activities to reduce wind erosion and dust generation during these activities. Haul areas will be wetted periodically to reduce fugitive dust along the designated haul routes.

Where expedited loading of excavated material is not implemented, material will be stockpiled within the work area. Stockpiled soils will be wetted as necessary to limit dust generation. Stockpiles that will remain in place over night will be protected from run-on and runoff through installation of BMPs at the completion of the work day.

Erosion mats, or equivalent BMP (e.g., mulch or tackifier) will be installed following excavation at areas to the west of Hurley on slopes equal or greater than 3:1 and in areas where concentrated flow is likely to occur, as specified by the field engineer. The mats will be rolled out and secured using metal or wooden stakes as specified by the manufacturer.

The excavation area to the north will not receive erosion mats as excavation will be completed at the caliche layer. Dust and wind erosion are not expected to be of concern in the north excavation area due to the presence of caliche. However, a tackifier will be applied to pockets of soil on top of caliche to maintain wind erosion control for any residual material remaining in the area. A tackifier is applied typically in the same manner as hydroseed – utilizing a spray application method. Tackifiers consist of a polymer that can be likened to soil glue and are utilized to control wind erosion from disturbed, exposed soil. A tackifier can be effective for a year following application. Seeding is typically done prior to application of the tackifier, where needed.

BMPs will be specified as part of the Stormwater General Permit Notice of Intent. Field modifications will be documented in the IRA Completion Report.

Chino will visually monitor seeded areas - as well as smaller areas with applied tackifier- following completion of the excavation activities. Should visible dusting of areas be noted, Chino will re-apply the tackifier and/or additional seeding as needed to control dust within the areas.

3.3.2 Worker and Residential Protection

The “Investigation Area Health and Safety Plan” (HASP) was developed for Chino in January 1997 to address and mitigate potential worker exposure during sampling and other site investigation-related activities. Levels of personnel protective equipment and monitoring during activities will be determined based on the 1997 HASP. A site-specific HASP will be developed prior to implementation of this Excavation IRASP.

The following are general requirements for monitoring during field activities.

All parties involved in the STSIU excavation will complete activities in accordance with the 1997 HASP and the site-specific HASP. Chino will assign a project Health & Safety (H&S) Officer for this activity, responsible for oversight of the H&S program. ARCADIS BBL and the Remediation Contractor will each assign a project team H&S leader to oversee field activities and ensure compliance with the HASPs.

The relevant issues applicable to property owners and residents will be communicated in a clear and effective manner prior to implementation of this Excavation IRASP.

The primary routes of exposure to site COCs are:

- Inhalation of particulate and dust generated during removal activities; and
- Incidental ingestion of constituents from direct contact with soil and dust, and from air emissions.

Site-specific engineering controls and monitoring will be employed to reduce exposures and ensure the safety of workers and residents during the excavation. Air monitoring will be conducted for compliance with New Mexico Air Quality standards within the excavation area and at the perimeter of each work area.

The air monitoring measures to be used for compliance are summarized below and are consistent with those employed during the Hurley residential dig (Golder, 2006):

- Ambient Air Monitoring – Ambient air monitors will be used to quantify dust levels, and determine whether off-site migration of dust occurs during excavation activities. The objective of ambient air monitoring is to be protective of residents in Hurley and on-site personnel. The data from these monitors will be reviewed daily for compliance against New Mexico Air Quality standards, and to monitor H&S action levels.
 - The NM air quality standards for total suspended particulate (TSP) are as follows:
 - 24-hour average – 150 $\mu\text{g}/\text{m}^3$;
 - 7-day average – 110 $\mu\text{g}/\text{m}^3$; and
 - Annual geometric mean average - 60 $\mu\text{g}/\text{m}^3$.

- **Personal Air Monitoring** – Personal air monitors will be used by field crews during the first week of remediation activities to collect air samples for total copper analysis, and other COCs as specified in the site-specific HASP to be developed for this removal action. The results from the personal monitors will be correlated with the ambient air monitors to determine whether worker exposures are above action levels, as described in the H&S Plan. If levels are satisfactory, personal air monitoring will be discontinued.
- **Dust Suppression** – The field crews will apply water to excavation, ground, and surfaces during excavation activities to reduce visible dust emissions.

Additional ambient air monitoring and dust monitoring procedures will be detailed in the site-specific Health and Safety Plan for this IRA which will be submitted as an appendix once the contractor is procured.

3.4 Post-Removal Confirmation Sampling

The purpose of post-removal confirmation sampling is to determine if the target cleanup goals have been met. As stated above, areas targeted for removal contain copper at concentrations greater than 5,000 ppm copper. However, areas will be removed and sampled to a target level of 2,700 ppm copper to address potential ecological risk.

Confirmation sampling will be conducted using X-Ray Florescence (XRF) field sampling methods. Sieved soil will be utilized per the XRF Sampling SOP. The XRF Sampling SOP is provided in Appendix A. The assumed error during field XRF sampling will be +/- 10% of the sample result. This tolerance should allow for confidence in removal areas. If a confirmation sample exceeds the target cleanup level, an additional 2-inch excavation will be performed, followed by another round of confirmation sampling at the same grid node as the original sample. This procedure will continue until all samples are below the target cleanup level.

3.4.1 Determination of Sample Size

The US Environmental Protection Agency (USEPA) guidance, “Methods for Evaluating the Attainment of Cleanup Standards” has been used to determine the number of samples required to demonstrate that 95% of the area sampled will be below the cleanup target of 2,700 ppm (vertical limits of removal) copper (EPA, 1989). The input parameters are listed in the following table.

TABLE 2
INPUT PARAMETERS FOR SAMPLE SIZE DETERMINATION

Parameter	Value	Description	Note
A	5%	False positive rate, gives 95% confidence.	5% chance of concluding area is clean when it is really still contaminated.
B	20%	False negative rate.	80% chance of concluding area is clean when it is really is clean.
P ₀	5%	Target percentage goal.	Conclude area is clean if less than 5% of samples exceed 2,700 ppm.
P ₁	2.5%	Assumed achieved percentage.	Assumed percent of samples exceeding goal of 2,700 ppm achieved after excavation.
n _d	384	Number of samples required.	Calculated value.

The sample size is determined using the following formula:

$$n_d = \left\{ \frac{z_{1-\beta} \sqrt{P_1(1-P_1)} + z_{1-\alpha} \sqrt{P_0(1-P_0)}}{P_0 - P_1} \right\}^2 \quad (7.1)$$

where $z_{1-\beta}$ and $z_{1-\alpha}$ are the critical values for the normal distribution with probabilities of $1-\alpha$ and $1-\beta$ (Table A.2).

Detailed calculations and table references for this function are provided in Appendix B.

Using the input parameters listed above and the USEPA function, a total of 384 samples is needed for confirmation that 95% of the area is below 2,700 ppm copper. The nature of the historic distribution of copper in these areas was via air dispersion in a predictable pattern decreasing in concentration from the source. Due to the nature of the disposition, a grid sample pattern is appropriate for the confirmation sampling. Figure 7 depicts the proposed confirmation sample locations over the excavation areas. The grid spacing is approximately 132 feet. A random point was selected for the initial grid location and subsequent grid sample locations were evenly spaced from the initially selected grid location. Grid nodes that fall on a non-soil (e.g., caliche) location will not be sampled (i.e., disregarded). The next following grid location will be marked and sampled per plan.

One sample in every 10 XRF samples (10%) will be collected as a field quality assurance (QA) sample and sent offsite for laboratory analysis by Silver Valley Laboratories (SVL) in Kellogg, Idaho. For each selected QA sample, the same sample fraction analyzed by XRF will be sent to the laboratory and analyzed for total copper using EPA Method 200.7 and soil paste pH using ASA Method Monograph 9.

XRF and confirmation laboratory sampling will be conducted in accordance with the policy, functional activities, and quality assurance/quality control (QA/QC) protocols, which are specifically stated in the RI Quality Assurance Plan (QAP) (Chino, 1997a). The QAP defines how site-wide QA/QC activities will be implemented during field sampling events. The objective of the QAP is to ensure that data are of adequate quality for its intended use. SOPs have been developed as part of the QAP and are incorporated by reference in this work plan. SOPs are attached as Appendix A to this work plan.

All sample locations will be surveyed for coordinate position and elevation using Global Positioning Systems (GPS). Sample locations will be located in the field using GPS and identified using stakes, flagging, or other appropriate means, and will be noted in field logbooks and/or soil sampling logs until they are sampled. Deviations from locations specified in this Excavation IRAWP will be documented in the Completion Report.

3.4.2 Field Sampling Methods

The following method will be used to collect soil samples for XRF analysis:

1. Equipment that will come in contact with the soil sample should be cleaned according to Field Equipment Cleaning-Decontamination SOP-6.
2. Use a decontaminated spade, spoon, scoop, macrocore, or hand auger to collect a sample over the required interval (0 to 2-inches below grade).
3. Use a ruler (or other measurement device) to verify that the sample is collected to the correct depth and record the top and bottom depths from the ground surface.

4. Backfill sample holes to grade with native material or other suitable material.
5. Decontaminate field equipment before proceeding to the subsequent sample location.

The following general SOPs will be utilized during this field program. In the case of discrepancies, the ARCADIS BBL SOPs will take precedence over QAP SOPs.

- Field Document Control (SOP-1) – Outlines the numbering scheme for field and laboratory samples. SOP-1 also presents procedures for recording information that is relevant to field operations.
- Field Logbook and Field Sample Data Sheets (SOP-2) – Identifies minimum entries to be included in field logbook or field sample data sheets. Includes procedures for taking photographs and labeling them.
- Field Quality Control (SOP-3) – Describes field QC measures and QC samples, including sample preparation and collection frequency.
- Sample Custody Procedures (SOP-4) – Establishes Chain-of-Custody procedures to be followed during field sample collection and transfer to the laboratory. Included are examples of a sample label, field sample data sheets, and a Chain-of-Custody record.
- Packaging and Shipping of Environmental Sample Containers (SOP-5) – Lists procedures for preparation and shipment of field samples sent to the analytical laboratory. Included is an example of a custody seal to be attached to each shipment.
- Decontamination of Equipment Used to Sample Soil and Water (SOP-6) – Presents the decontamination requirements for non-disposable sampling equipment. Included is a list of recommended equipment to be used for decontamination. Disposable equipment will be used to the extent possible to reduce opportunities for cross-contamination and decrease the level of effort for decontamination. For reusable field equipment, decontamination is required to prevent cross-contamination of samples from different sampling locations. A modification to SOP – 6 eliminated the use of a nitric wash.
- Requesting Environmental Laboratory Services (SOP-7) – SVL of Kellogg, Idaho will be contracted by Chino to provide laboratory services. Provided in this SOP is a form for requesting analyses, including number of samples, proposed schedule and designated contact.
- Sampling, Preservation and Containerization (SOP-14) - This SOP describes the techniques and quality control measures used to sample, prepare, and handle soil subject to the specified analyses.
- Procedures for Metals Analysis Using Field Portable X-Ray Fluorescence Analyzers (SOP-23a) - This SOP describes the techniques and quality control measures used to field-analyze the collected soil samples.

EPA method 6200 presents a method for determining the quality of in situ testing obtained by XRF. This method for determining quality of in situ testing also applies to intrusive testing with minimal sample preparation. The method is summarized below (Sackett et al. 1998).

Direct comparison of in situ or intrusive testing to laboratory testing

- Plot the XRF data on the y-axis and the laboratory data on the x-axis for the selected QA/QC samples.
- Determine the linear relationship of the data ($y=mx$).
- Specify the correction factor (m) for the XRF data.
- Determine the correlation factor (R^2).

The second portion of EPA 6200 addresses quality of field sampling. The following analysis will be performed at a rate of 10%, or a total of 80 locations.

Stepwise sample preparation to determine data quality of in situ or intrusive testing

- Delineate a region of soil approximately 4" x 4".
- Perform several in-situ tests in this area, or collect the top (approximately) quarter inch of soil from this region, bag the soil, test through the bag. In either case, average the results.
- If you did not bag the in-situ test sample, collect the top (approximately) quarter inch of soil from this region and sieve through the 2 mm sieve that is provided with the instrument. Otherwise sieve the bagged sample used for the in-situ test. Thoroughly mix the sieved sample, and place some of the sieved material into an XRF cup, and perform a test of this sample.
- If the results of this prepared sample differ less than 20% with the average in-situ result, this indicates the soil in this region is reasonably homogeneous. The data quality in this case is probably at the semi-quantitative level, rather than just screening data.
- If the results differ by more than 20%, this indicates the soil is not very homogeneous, and there are serious particle size effects affecting your in-situ measurements.
- In this case, sieve the sample through the 250 μ m sieve. Mix this sample and place a sub-sample into an XRF cup for testing. If this result differs from the previous by less than 20% then this indicates that at a minimum the 2mm sieving is necessary to achieve higher data quality.
- If this result differs by more than 20% from the sample sieved through 2 mm, then particle size effects are still affecting the XRF result. In this case, samples should be sieved through 125 μ m to assure data quality at the quantitative level. Sieving through the 125 μ m is typically adequate to assure a quantitative data quality level.

3.5 Revegetation

Revegetation of the disturbed areas will serve the purpose of a BMP to limit erosion and provide for dust control within the disturbed areas. Disturbed areas will be vegetated using the seed mixture presented in the Closure/Closeout plan as guidance (Table 3). The restored areas will be inspected periodically following final grading and restoration for establishment of vegetation as a BMP for erosion and dust control. Quarterly inspections will be conducted to review density and type of vegetation reestablished within the areas for one year following excavation. Thereafter, vegetation inspections would be conducted annually for four additional years. Following 5 years of monitoring, Chino will submit a vegetation monitoring report to NMED with recommendations either for continued monitoring or for cessation of monitoring based on re-establishment of the plant community and coverage within the disturbed areas.

Following soil removal within the highway ROW, Chino will apply interim measures (e.g., tackifier or hydroseeding) for dust control until the highway expansion project occurs. Should the expansion not occur within 6 months of application of interim measures, Chino will reseed the area and begin monitoring of the revegetation.

Additional monitoring may not necessary in the area since it will have been returned to a "natural state" following restoration. The objective of this removal action is to excavate the impacted soil and restore the areas

to pre-excavation conditions. Revegetation is a BMP for controlling dust following soil disturbance. Extensive long-term monitoring should not necessary to accomplish this objective.

TABLE 3
PROPOSED SEED MIX AND APPLICATION RATES

Species	Life-Form	Duration	Seasonality	Rate
Blue grama (<i>Bouteloua gracilis</i>)	Grass	Per	Warm	0.25
Sied-oats grama (<i>Bouteloua curtipendula</i>)	Grass	Per	Warm	1.25
Black grama (<i>Bouteloua eripoda</i>)	Grass	Per	Warm	0.10
Green sprangletop (<i>Leptochloa dubia</i>)	Grass	Per	Warm	0.15
Plains lovegrass (<i>Eragrostis intermedia</i>)	Grass	Per	Intermediate	0.05
Bottlebrush squirreltail (<i>Sitanion hystrix</i>)	Grass	Per	Cool	1.25
New Mexico needlegrass (<i>Stipa neomexicana</i>)	Grass	Per	Cool	1.75
Streambank wheatgrass (<i>Agropyron distachyum</i> v. <i>riparium</i>)	Grass	Per	Cool	1.50
Apache plume (<i>Fallugia pardoxa</i>)	Shrub	Per	NA	0.10
Rubber rabbitbush (<i>Chrysothamnus nauseosus</i>)	Shrub	Per	NA	0.05
Winterfat (<i>Eurotia lanata</i>)	Shrub	Per	NA	0.60
Yellow sweet clover (<i>Melilotus officinalis</i>)	Forb	Ann	NA	0.14
Globe mallow (<i>Sphaeralcea</i> sp.)	Forb	Per	NA	0.10
Blue flax (<i>Linum lewisii</i>)	Forb	Per	NA	0.15
Total PLS (lb/ac)				7.45

Notes:

per = perennial; ann = annual

Rate is in pounds of pure live seed (PLS) per acre (lb/ac); substitutions may change seeding rates

NA = not applicable

Seed mix and rates are subject to change based on future investigations

3.6 Construction Documentation

A Completion Report will be prepared and submitted to NMED following site work. The following information will be documented during field implementation and included in the Completion Report:

- Documentation of construction methods and sequencing;
- Documentation of TCLP samples from stockpiled materials;
- Interim and Completed grades;
- Photo documentation;
- Field modifications;
- Dust monitoring calibration and sample data;
- Confirmation sample locations and results; and
- Final volume and extent of excavation.

The Completion Report will be prepared and submitted for NMED review and approval within 90 days of completion of field activities.

3.7 Project Schedule

Project schedule will be heavily dependent on machinery selected and number of crews running concurrently for removal actions. Project duration is assumed to be between 2 and 4 months, depending on construction methods employed.

Brief monthly status reports will be delivered to NMED during the field activities. The status reports will, in general, include the following topics:

- Updated project schedule and estimated completion date;
- Field modifications;
- Percent complete; and
- A discussion of any unanticipated items.

As noted above, the Completion Report will be prepared after site removal activities are completed.

4.0 Regulatory Review

Activities associated with the interim remedial action described in Section 3 must comply with regulatory and permit requirements governing the site. This section outlines appropriate, relevant, and applicable requirements (ARARs) for permitting and regulatory requirements for this removal action. These include a National Pollutant Discharge Elimination System (NPDES) Construction General Permit (CGP) (which includes preparation of a Storm Water Pollution Prevention Plan (SWPPP) and a Best Management Plan), endangered species regulations (which may include preparation of an Incidental Take Permit), Total Maximum Daily Load (TMDL) requirements, and coordination with New Mexico Department of Transportation (NMDOT) and the rail road for excavation in or near their right-of-ways. Also required is a modification request under DP 214 to allow placement of the excavated soils into Tailing Pond 1. General requirements of as well as means for compliance with these permits are described in the following sections.

4.1 NPDES Construction General Permit

The NPDES-Construction General Permit (CGP) is required for all construction projects that disturb one or more acres of land and applies to activities such as soil disturbances, clearing, grading, and excavation. The NPDES-CGP permit must be applied for by the responsible party and approved prior to beginning work. Site activities must comply with the SWPPP and Best Management Plan developed by Chino, endangered species protection requirements (Section 4.2) and Total Maximum Daily Limits (TMDL) requirements (Section 4.3).

Application for an NPDES-CGP includes posting a Notice of Intent (NOI), as well as developing a SWPPP and Best Management Plan. The NOI must be posted on the EPA's NOI Search Page seven days prior to starting construction. Specific instructions for completing the NOI are available on the U.S. EPA NPDES website (www.cfpub.epa.gov/npdes). An example NOI application form is provided in Appendix C. Guidelines for completing the SWPPP and Best Management Plan are provided in Appendix C.

The NOI and SWPPP will be prepared as part of the planning portion of this work. These documents will be submitted for review and approval at least 45 days prior to implementation of this Excavation IRAWP.

4.2 Endangered Species Requirements

In order to perform work under a NPDES-CGP permit, the presence of endangered or threatened species or critical habitat at the site must be evaluated. The endangered species list for Grant County will be reviewed, and, if endangered or threatened species or critical habitats are determined to exist on site, the U.S. Fish and Wildlife Service (FWS) will be contacted. If no protected species or habitat is present further action is not required and the CGP adequately fulfills permit requirements. If protected species or habitat is present, storm water discharge or discharge-related activities must be evaluated to determine if there is potential to adversely affect protected species or habitat. If discharge may affect protected species or habitat, action to avoid protected species or habitat impact must be taken in compliance with Criterion B, C, D, or F of Subpart 1.3.C.6 of the CGP and approved by the FWS, which may include applying for an Incidental Take Permit (ITP).

4.3 Total Maximum Daily Loads Requirements

CGP requirements include compliance with TMDL regulations. TMDL is determined for runoff and discharge related to construction, industrial, or storm water from the site during construction activities. TMDL

requirements will be considered and included in the SWPPP. Guidelines for determining acceptable TMDL are available by contacting the NMED.

4.4 State Historic Preservation Office

Chino Mines site not listed on State or National Historic Register and is therefore not regulated by the State Historic Preservation Office. As part of Chino's internal BMP requirements, a pedestrian archeological survey will be conducted prior to implementation of this Excavation IRAWP.

4.5 Discharge Plan

Chino will file for a permit modification for Discharge Plan 214 to account for placement of excavated materials at Tailing Pond 1 as proposed in this Excavation IRAWP.

4.6 Highway and Rail Road Right-of-Way

Chino will coordinate working in or near the right-of-way for the highway with the NMDOT. Excavation areas may be adjusted following discussions with NMDOT based on right of way distances and access agreements. Removal areas have been defined in this IRAWP based on a 50-foot buffer from the railroad.

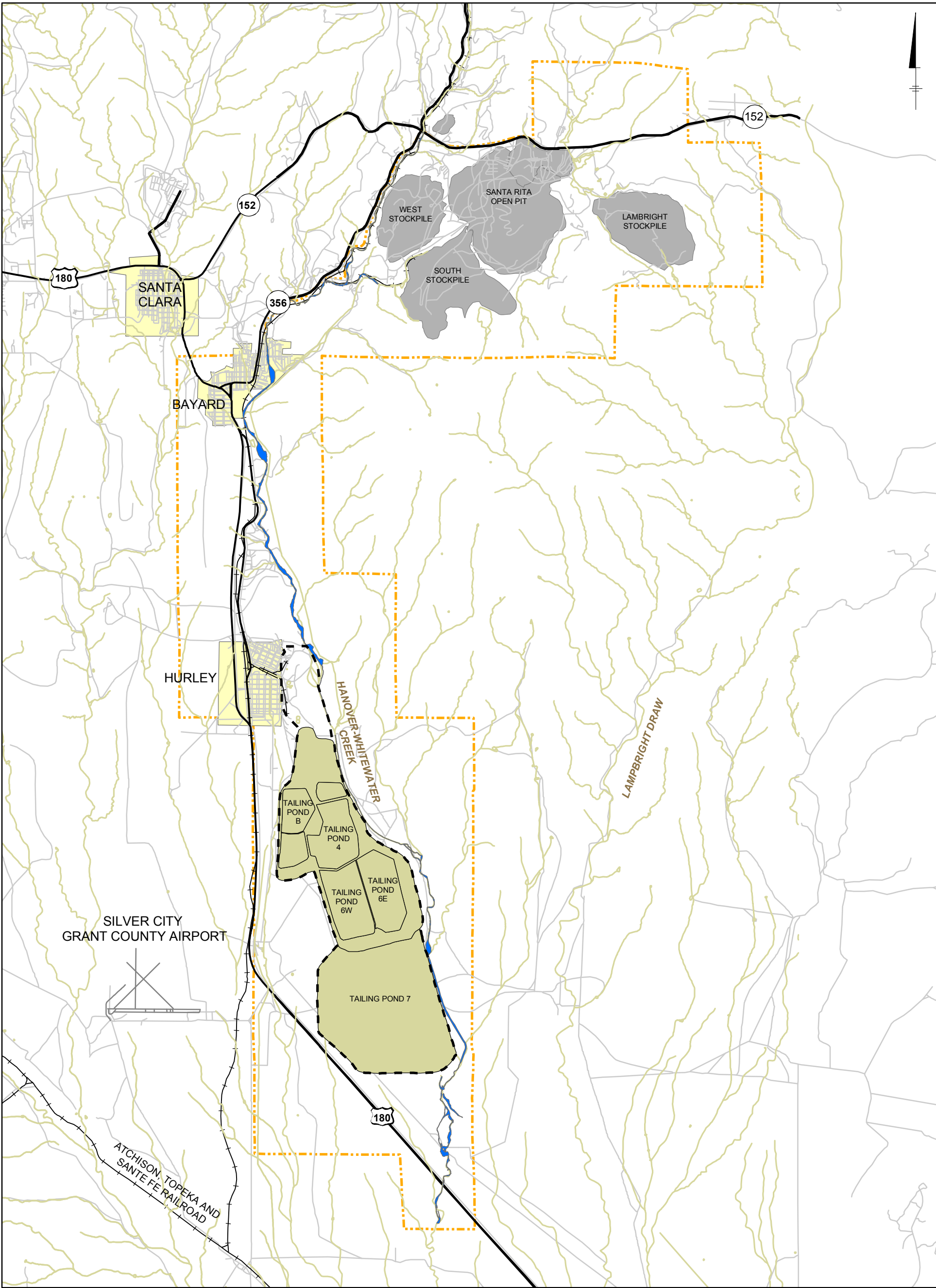
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
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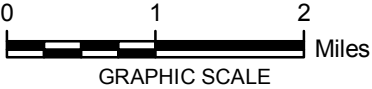
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FIGURES



LEGEND:

- | | | | |
|---|----------------|---|-----------------------------------|
|  | ACTIVE CHANNEL |  | AOC BOUNDARY |
|  | STOCKPILES |  | DRAINAGE |
|  | TAILING PONDS |  | SMLTER / TAILING OPERATIONAL AREA |
|  | CITY LIMITS | | |

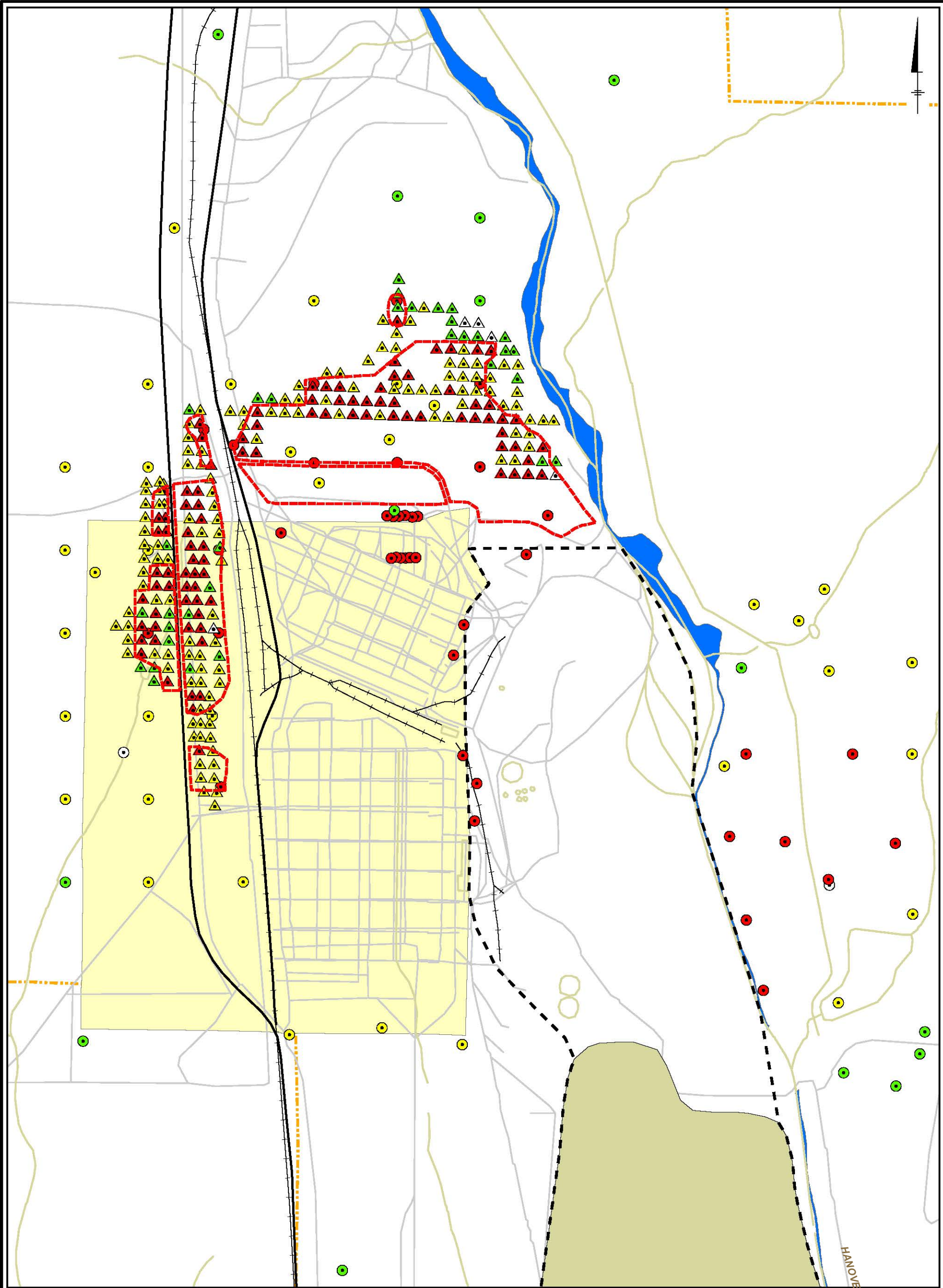


CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

SITE LOCATION MAP



FIGURE
1



LEGEND:
Cu CONCENTRATIONS (mg/kg)

HISTORIC	GOLDER 2007
0 to 500	0 to 500
500 to 2000	500 to 2000
2000 to 5000	2000 to 5000
5000+	5000+

--- APPROXIMATE REMOVAL AREA
WITH SOIL COPPER > 5,000 MG/KG

TAILING PONDS
CITY LIMITS
AOC BOUNDARY
DRAINAGE
SMELTER / TAILING
OPERATIONAL AREA

NOTE:
SOURCES INCLUDE CHINO (1995),
ARCADIS JSA (2001), AND SRK (2005).

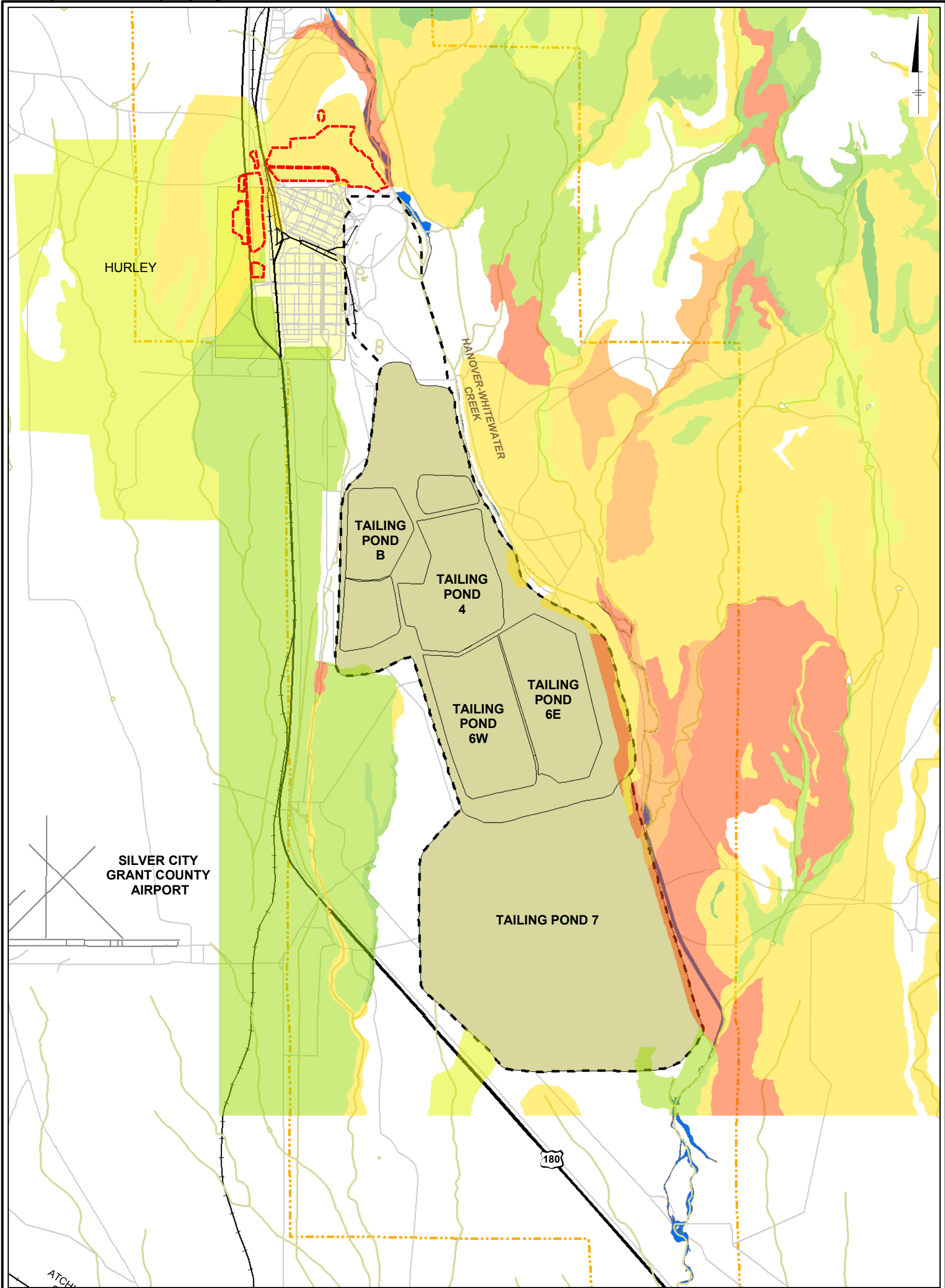
0 1,000 2,000
Feet
GRAPHIC SCALE

CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

SAMPLE DATA

ARCADIS BBL
Infrastructure, environment, facilities

FIGURE
2



LEGEND:

RANGELAND CONDITIONS

- EXCELLENT
- EXCELLENT - GOOD
- GOOD
- GOOD - FAIR
- FAIR
- FAIR-POOR
- POOR
- UNDEFINED

APPROXIMATE REMOVAL AREA
WITH SOIL COPPER > 5,000 MG/KG

- TAILING PONDS
- CITY LIMITS
- AOC BOUNDARY
- DRAINAGE
- SMELTER / TAILING OPERATIONAL AREA



CHINO MINES COMPANY
HURLEY, NM
STSIU IRAW

RANGELAND CONDITIONS



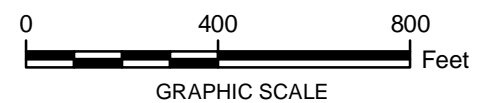
FIGURE
3

09/22/06 PET-85 EGH NYC-85 TBR
Chino Mines Company (63624.001)
Q:\PhelpsDodge\Chino\STSIU IRAWP\Mxd\Fig. 4 NorthDetail.mxd



LEGEND:

- 5 FT. CONTOURS
- - - APPROXIMATE REMOVAL AREA
WITH SOIL COPPER > 5,000 MG/KG



CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

**LIMITS OF EXCAVATION -
NORTH DETAIL AREA**



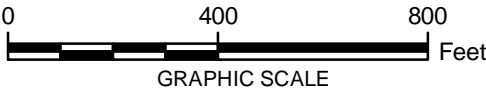
FIGURE
4



LEGEND:

— 5 FT. CONTOURS

--- APPROXIMATE REMOVAL AREA
WITH SOIL COPPER > 5,000 MG/KG

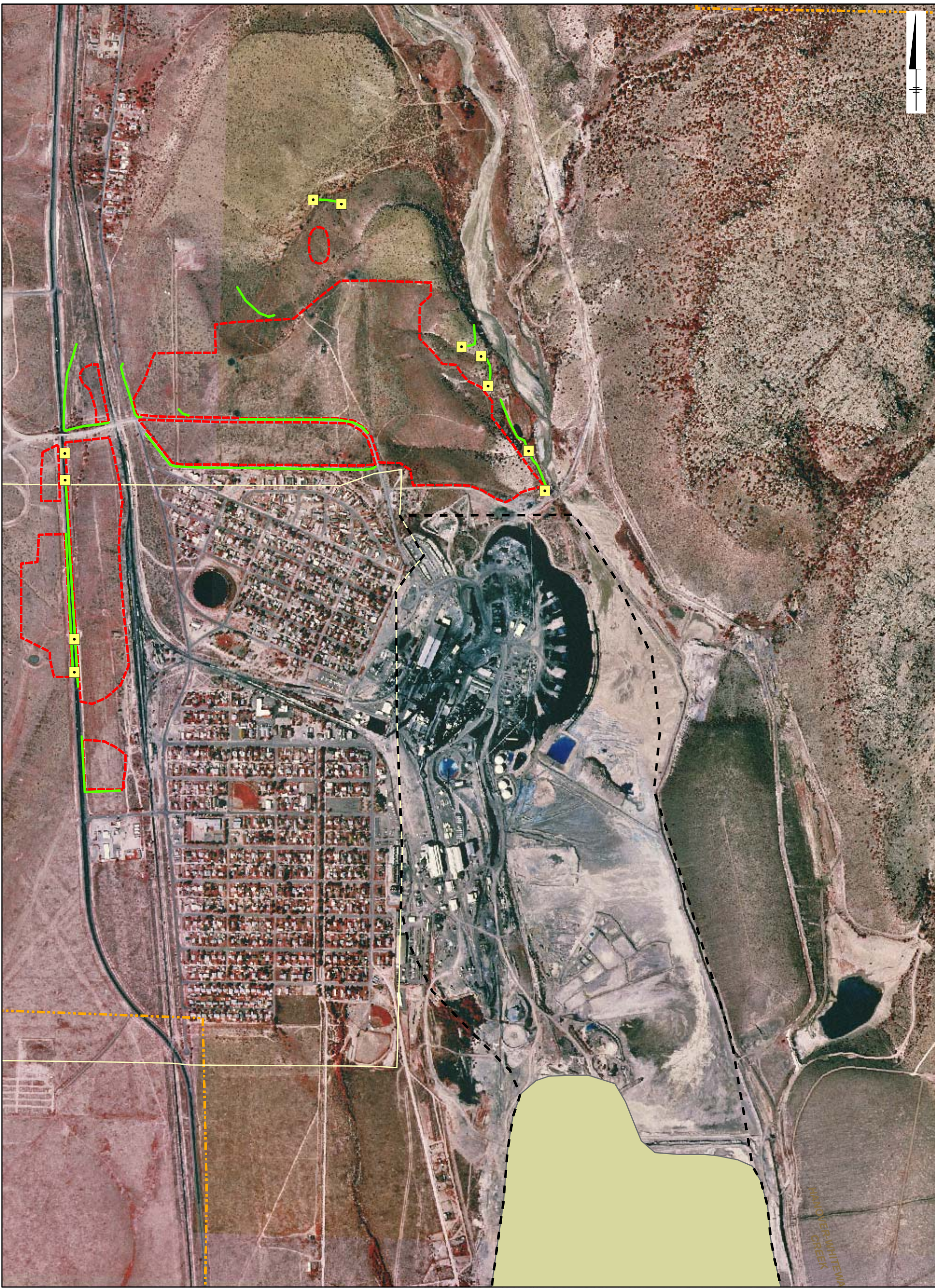


CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

LIMITS OF EXCAVATION - WEST DETAIL AREA

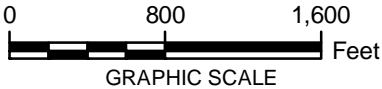


FIGURE 5



LEGEND:

- LOCATION OF STRAW BALES
- SILT FENCES
- CITY LIMITS
- AOC BOUNDARY
- APPROXIMATE REMOVAL AREA WITH SOIL COPPER > 5,000 MG/KG
- SMELTER / TAILING OPERATIONAL AREA

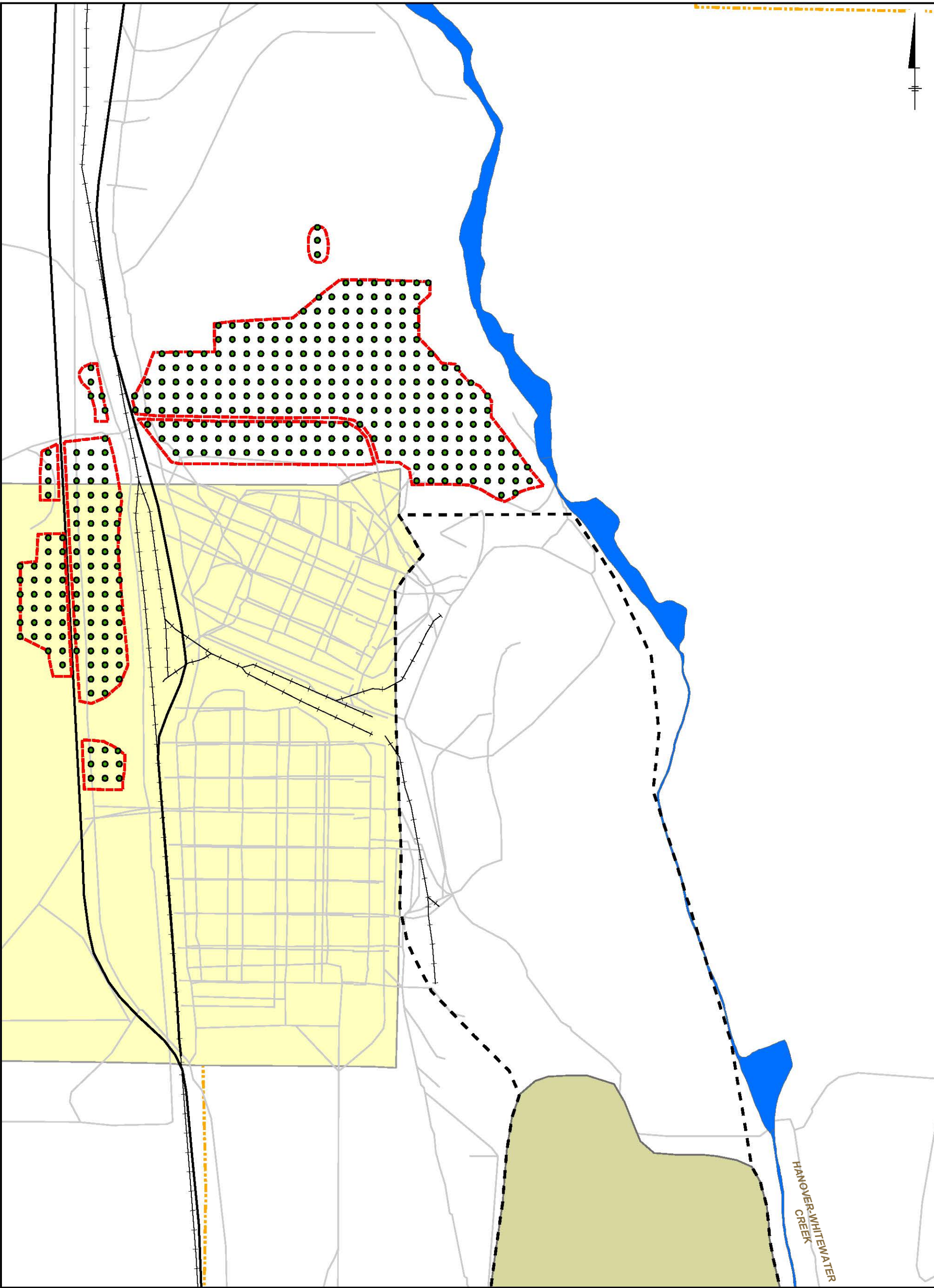


CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

BEST MANAGEMENT PRACTICES

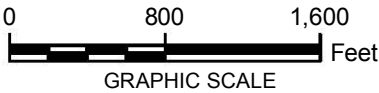


FIGURE
6



LEGEND:

- CONCEPTUAL CONFIRMATION SAMPLING GRID
- TAILING PONDS
- CITY LIMITS
- AOC BOUNDARY
- APPROXIMATE REMOVAL AREA WITH SOIL COPPER > 5,000 MG/KG
- SMELTER / TAILING OPERATIONAL AREA



CHINO MINES COMPANY
HURLEY, NM
STSIU IRAWP

CONFIRMATION SAMPLE LOCATIONS



FIGURE
7

APPENDICES

Appendix A

EPA Method 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE
DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed in Table 1 for soil and sediment samples. Some common elements are not listed in Table 1 because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). They are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed in Table 1 are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF.

1.2 Detection limits depend on several factors, the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. General instrument detection limits for analytes of interest in environmental applications are shown in Table 1. These detection limits apply to a clean matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (600-second) count times. These detection limits are given for guidance only and will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of field performance-based detection limits is presented in Section 13.4 of this method. The clean matrix and field performance-based detection limits should be used for general planning purposes, and a third detection limit discussed, based on the standard deviation around single measurements, should be used in assessing data quality. This detection limit is discussed in Sections 9.7 and 11.3.

1.3 Use of this method is restricted to personnel either trained and knowledgeable in the operation of an XRF instrument or under the supervision of a trained and knowledgeable individual. This method is a screening method to be used with confirmatory analysis using EPA-approved methods. This method's main strength is as a rapid field screening procedure. The method detection limits (MDL) of FPXRF are above the toxicity characteristic regulatory level for most RCRA analytes. If the precision, accuracy, and detection limits of FPXRF meet the data quality objectives (DQOs) of your project, then XRF is a fast, powerful, cost effective technology for site characterization.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. X-ray tubes are used to irradiate samples in the laboratory and are beginning to be incorporated into field portable instruments. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This later process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons

results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples: the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (β), which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.7 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments: in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

3.1 FPXRF: Field portable x-ray fluorescence.

3.2 MCA: Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS: Site specific calibration standard.

3.4 FP: Fundamental parameter.

3.5 ROI: Region of interest.

3.6 SRM: Standard reference material. A standard containing certified amounts of metals in soil or sediment.

3.7 eV: Electron Volt. A unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One and Chapter Three for additional definitions.

4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup, the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the K_{β} line of element Z-1 with the K_{α} line of element Z. This is called the K_{α}/K_{β} interference. Because the $K_{\alpha}:K_{\beta}$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_{α} and K_{β} energies are 4.95

and 5.43 keV, respectively, and the Cr K_{α} energy is 5.41 keV. The Fe K_{α} and K_{β} energies are 6.40 and 7.06 keV, respectively, and the Co K_{α} energy is 6.92 keV. The difference between the V K_{β} and Cr K_{α} energies is 20 eV, and the difference between the Fe K_{β} and the Co K_{α} energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_{α} /lead (Pb) L_{α} and sulfur (S) K_{α} /Pb M_{α} . In the As/Pb case, Pb can be measured from the Pb L_{β} line, and As can be measured from either the As K_{α} or the As K_{β} line; in this way the interference can be corrected. If the As K_{β} line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_{α} line. If the As K_{α} line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in no As being reported regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis by an EPA-approved method.

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as SW-846 Method 3050, or a total digestion procedure, such as Method 3052 is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project data quality objectives.

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method, the confirmatory method used was Method 3050, and the FPXRF data

compared very well with regression correlation coefficients (r^2 often exceeding 0.95, except for barium and chromium. See Table 9 in Section 17.0). The critical factor is that the digestion procedure and analytical reference method used should meet the data quality objectives (DQOs) of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Section 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10 to 20°F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operators manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. Licenses for radioactive materials are of two types; (1) general license which is usually provided by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) specific license which is issued to named persons for the operation of radioactive instruments as required by local state agencies. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals. A copy of the radioactive material licenses and leak tests should be present with the instrument at all times and available to local and national authorities upon request. X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. Finally, an additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply. The danger of electric shock is as substantial as the danger from radiation but is often overlooked because of its familiarity.

5.2 Radiation monitoring equipment should be used with the handling of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs should be worn in the area of most frequent exposure. The maximum permissible whole-body dose from occupational exposure is 5

Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

5.3 Refer to Chapter Three for guidance on some proper safety protocols.

6.0 EQUIPMENT AND SUPPLIES

6.1 FPXRF Spectrometer: An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation Sources: Most FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron (Fe)-55, cadmium (Cd)-109, americium (Am)-241, and curium (Cm)-244. These sources may be contained in a probe along with a window and the detector; the probe is connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum required for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic

x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of accelerating voltage is governed by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample Presentation Device: FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For most FPXRF instruments operated in the intrusive mode, the probe is rotated so that the window faces upward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors: The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide (HgI_2), silicon pin diode and lithium-drifted silicon $\text{Si}(\text{Li})$. The HgI_2 detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The $\text{Si}(\text{Li})$ detector must be cooled to at least -90°C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a $\text{Si}(\text{Li})$ detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 liter. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese K_α peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: HgI_2 -270 eV; silicon pin diode-250 eV; $\text{Si}(\text{Li})$ -170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data Processing Units: The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in parts per million on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 100 to 500 sets of numerical analytical results. Most FPXRF

instruments are menu-driven from software built into the units or from PCs. Once the data-storage memory of an FPXRF unit is full, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery chargers.

6.3 Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film: Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 micrometers (μm) thick.

6.5 Mortar and pestle: glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers: glass or plastic to store samples.

6.7 Sieves: 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels: for smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags: used for collection and homogenization of soil samples.

6.10 Drying oven: standard convection or toaster oven, for soil and sediment samples that require drying.

7.0 REAGENTS AND STANDARDS

7.1 Pure Element Standards: Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if required for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.2 Site-specific Calibration Standards: Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.2.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of ten samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.2.2 Each sample should be oven-dried for 2 to 4 hours at a temperature of less than 150°C. If mercury is to be analyzed, a separate sample portion must remain undried, as heating may volatilize the mercury. When the sample is dry, all large, organic debris and

nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be ground with a mortar and pestle and passed through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.2.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 grams of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 grams of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.3 Blank Samples: The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the method detection limits. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.4 Standard Reference Materials: Standard reference materials (SRM) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, Inorganic Analytes.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance protocols. All field data sheets and quality control data should be maintained for reference or inspection.

9.2 Energy Calibration Check: To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting, which would indicate drift within the instrument. As discussed in Section 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (> 10 to 20°F).

The energy calibration check should be run at a frequency consistent with manufacturers recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.1 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak.

The intensity and channel number of the pure element as measured using the radioactive source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank Samples: Two types of blank samples should be analyzed for FPXRF analysis: instrument blanks and method blanks. An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window.

9.3.1 The instrument blank can be silicon dioxide, a Teflon block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the method detection limits should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. To be acceptable, a method blank must not contain any analyte at a concentration above its method detection limit. If an analyte's concentration exceeds its method detection limit, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration Verification Checks: A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ± 20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision Measurements: The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It

is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent.

The equation for calculating RSD is as follows:

$$\text{RSD} = (\text{SD}/\text{Mean Concentration}) \times 100$$

where:

RSD	=	Relative standard deviation for the precision measurement for the analyte
SD	=	Standard deviation of the concentration for the analyte
Mean Concentration	=	Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the detection limit, but decreases sample throughput.

9.6 Detection Limits: Results for replicate analyses of a low-concentration sample, SSCS, or SRM can be used to generate an average site-specific method detection and quantitation limits. In this case, the method detection limit is defined as 3 times the standard deviation of the results for the low-concentration samples and the method quantitation limit is defined as 10 times the standard deviation of the same results. Another means of determining method detection and quantitation limits involves use of counting statistics. In FPXRF analysis, the standard deviation from counting statistics is defined as $\text{SD} = (N)^{1/2}$, where SD is the standard deviation for a target analyte peak and N is the net counts for the peak of the analyte of interest (i.e., gross counts minus background under the peak). Three times this standard deviation would be the method detection limit and 10 times this standard deviation would be the method quantitation limit. If both of the above mentioned approaches are used to calculate method detection limits, the larger of the standard deviations should be used to provide the more conservative detection limits.

This SD based detection limit criteria must be used by the operator to evaluate each measurement for its useability. A measurement above the average calculated or manufacturer's detection limit, but smaller than three times its associated SD, should not be used as a quantitative measurement. Conversely, if the measurement is below the average calculated or manufacturer's detection limit, but greater than three times its associated SD. It should be coded as an estimated value.

9.7 Confirmatory Samples: The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared

sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r^2) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r^2 is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Calibration: Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental Parameters Calibration: FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are required, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are required.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Section 7.2. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective Energy FP Calibration: The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured

x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

10.2.2 BFP Calibration: BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the

calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical Calibration: An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Section 7.2; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is required. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are required to perform an adequate empirical calibration. The number of required standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton Normalization Method: The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline interference. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton K_{α} peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later on in analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, one requirement is that any large or nonrepresentative debris be removed from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Another requirement is that the soil surface be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide data for this method, this modest amount of sample preparation was found to take less than 5 minutes per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for *in situ* analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on required detection limits.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 grams or 250 cm³, which is enough soil to fill an 8-ounce jar. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Section 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the homogenization procedure using the fluorescein dye required 3 to 5 minutes per sample. As demonstrated in Sections 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, it can be used without the more labor intensive steps of drying, grinding, and sieving given in Sections 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps must be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 grams) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hours in the convection or toaster oven at a temperature not greater than 150°C. Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 minutes per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle,

and sieves must be thoroughly cleaned so that any cross-contamination is below the MDLs of the procedure or DQOs of the analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in parts per million and can be downloaded to a PC, which can provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation.

13.0 METHOD PERFORMANCE

13.1 This section discusses four performance factors, field-based method detection limits, precision, accuracy, and comparability to EPA-approved methods. The numbers presented in Tables 4 through 9 were generated from data obtained from six FPXRF instruments. The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from nondetect to tens of thousands of mg/kg.

13.2 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI₂ detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.3 All data presented in Tables 4 through 9 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.4 Field-Based Method Detection Limits: The field-based method detection limits are presented in Table 4. The field-based method detection limits were determined by collecting ten replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected method detection limits. Based on these ten replicate measurements, a standard deviation on the replicate analysis was calculated. The method detection limits presented in Table 4 are defined as 3 times the standard deviation for each analyte.

The field-based method detection limits were generated by using the count times discussed earlier in this section. All the field-based method detection limits were calculated for soil samples that had been dried and ground and placed in a sample cup with the exception of the MAP Spectrum Analyzer. This instrument can only be operated in the in situ mode, meaning the samples were moist and not ground.

Some of the analytes such as cadmium, mercury, silver, selenium, and thorium were not detected or only detected at very low concentrations such that a field-based method detection limit could not be determined. These analytes are not presented in Table 4. Other analytes such as calcium, iron, potassium, and titanium were only found at high concentrations (thousands of mg/kg) so that reasonable method detection limits could not be calculated. These analytes also are not presented in Table 4.

13.5 Precision Measurements: The precision data is presented in Table 5. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from nondetects to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 5 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the MDL for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 5. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the MDLs so that an RSD value calculated at 5 to 10 times the MDL was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 6 shows these results. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the detection limit of the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the *in situ* homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 6 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square, measurements of different soil samples were actually taking place within the square. Table 6 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five versus ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy Measurements: Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 7 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 7 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 7. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 7.

Table 8 provides a more detailed summary of accuracy data for one FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. Table 8 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability: Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination (r^2).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 9. Similar trends in the data were seen for all instruments.

Table 9 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--in situ, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not ground; and preparation 4--sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with r^2 values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The r^2 values and slopes of the regression lines for barium and chromium were

not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 9 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 9 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Section 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time required to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 minutes. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 minutes per sample. Lastly, when grinding and sieving is conducted, time must be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 Hewitt, A.D. 1994. "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_{α} Peak Normalization Analysis." *American Environmental Laboratory*. Pages 24-32.

13.8.2 Piorek, S., and J.R. Pasmore. 1993. "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer." *Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals*. Las Vegas, Nevada. February 24-26, 1993. Volume 2, Pages 1135-1151.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Metorex. X-MET 920 User's Manual.
2. Spectrace Instruments. 1994. Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction.
3. TN Spectrace. Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.
4. Unpublished SITE data, recieved from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 9 and a method procedure flow diagram.

TABLE 1
INTERFERENCE FREE DETECTION LIMITS

Analyte	Chemical Abstract Series Number	Detection Limit in Quartz Sand (milligrams per kilogram)
Antimony (Sb)	7440-36-0	40
Arsenic (As)	7440-38-0	40
Barium (Ba)	7440-39-3	20
Cadmium (Cd)	7440-43-9	100
Calcium (Ca)	7440-70-2	70
Chromium (Cr)	7440-47-3	150
Cobalt (Co)	7440-48-4	60
Copper (Cu)	7440-50-8	50
Iron (Fe)	7439-89-6	60
Lead (Pb)	7439-92-1	20
Manganese (Mn)	7439-96-5	70
Mercury (Hg)	7439-97-6	30
Molybdenum (Mo)	7439-93-7	10
Nickel (Ni)	7440-02-0	50
Potassium (K)	7440-09-7	200
Rubidium (Rb)	7440-17-7	10
Selenium (Se)	7782-49-2	40
Silver (Ag)	7440-22-4	70
Strontium (Sr)	7440-24-6	10
Thallium (Tl)	7440-28-0	20
Thorium (Th)	7440-29-1	10
Tin (Sn)	7440-31-5	60
Titanium (Ti)	7440-32-6	50
Vanadium (V)	7440-62-2	50
Zinc (Zn)	7440-66-6	50
Zirconium (Zr)	7440-67-7	10

Source: References 1, 2, and 3

TABLE 2
SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

Source	Activity (mCi)	Half-Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe-55	20-50	2.7	5.9	Sulfur to Chromium Molybdenum to Barium	K Lines L Lines
Cd-109	5-30	1.3	22.1 and 87.9	Calcium to Rhodium Tantalum to Lead Barium to Uranium	K Lines K Lines L Lines
Am-241	5-30	458	26.4 and 59.6	Copper to Thulium Tungsten to Uranium	K Lines L Lines
Cm-244	60-100	17.8	14.2	Titanium to Selenium Lanthanum to Lead	K Lines L Lines

Source: Reference 1, 2, and 3

TABLE 3
SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

Anode Material	Recommended Voltage Range (kV)	K-alpha Emission (keV)	Elemental Analysis Range	
Cu	18-22	8.04	Potassium to Cobalt Silver to Gadolinium	K Lines L Lines
Mo	40-50	17.4	Cobalt to Yttrium Europium to Radon	K Lines L Lines
Ag	50-65	22.1	Zinc to Technicium Ytterbium to Neptunium	K Lines L Lines

Source: Reference 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4
FIELD-BASED METHOD DETECTION LIMITS (mg/kg)^a

Analyte	Instrument					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	55	NR	NR	NR	NR	NR
Arsenic	60	50	55	50	110	225
Barium	60	NR	30	400	NR	NR
Chromium	200	460	210	110	900	NR
Cobalt	330	NR	NR	NR	NR	NR
Copper	85	115	75	100	125	525
Lead	45	40	45	100	75	165
Manganese	240	340	NR	NR	NR	NR
Molybdenum	25	NR	NR	NR	30	NR
Nickel	100	NR	NA	NA	NA	NR
Rubidium	30	NR	NR	NR	45	NR
Strontium	35	NR	NR	NR	40	NR
Tin	85	NR	NR	NR	NR	NR
Zinc	80	95	70	NA	110	NA
Zirconium	40	NR	NR	NR	25	NR

Source: Reference 4

^a MDLs are related to the total number of counts taken. See Section 13.3 for count times used to generate this table.

NR Not reported.

NA Not applicable; analyte was reported but was not at high enough concentrations for method detection limit to be determined.

**TABLE 5
PRECISION**

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the MDL					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	6.54	NR	NR	NR	NR	NR
Arsenic	5.33	4.11	3.23	1.91	12.47	6.68
Barium	4.02	NR	3.31	5.91	NR	NR
Cadmium	29.84 ^a	NR	24.80 ^a	NR	NR	NR
Calcium	2.16	NR	NR	NR	NR	NR
Chromium	22.25	25.78	22.72	3.91	30.25	NR
Cobalt	33.90	NR	NR	NR	NR	NR
Copper	7.03	9.11	8.49	9.12	12.77	14.86
Iron	1.78	1.67	1.55	NR	2.30	NR
Lead	6.45	5.93	5.05	7.56	6.97	12.16
Manganese	27.04	24.75	NR	NR	NR	NR
Molybdenum	6.95	NR	NR	NR	12.60	NR
Nickel	30.85 ^a	NR	24.92 ^a	20.92 ^a	NA	NR
Potassium	3.90	NR	NR	NR	NR	NR
Rubidium	13.06	NR	NR	NR	32.69 ^a	NR
Strontium	4.28	NR	NR	NR	8.86	NR
Tin	24.32 ^a	NR	NR	NR	NR	NR
Titanium	4.87	NR	NR	NR	NR	NR
Zinc	7.27	7.48	4.26	2.28	10.95	0.83
Zirconium	3.58	NR	NR	NR	6.49	NR

Source: Reference 4

^a These values are biased high because the concentration of these analytes in the soil samples was near the detection limit for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the method detection limit.

TABLE 6
PRECISION AS AFFECTED BY SAMPLE PREPARATION

Analyte	Average Relative Standard Deviation for Each Preparation Method		
	In Situ-Field	Intrusive- Undried and Unground	Intrusive- Dried and Ground
Antimony	30.1	15.0	14.4
Arsenic	22.5	5.36	3.76
Barium	17.3	3.38	2.90
Cadmium ^a	41.2	30.8	28.3
Calcium	17.5	1.68	1.24
Chromium	17.6	28.5	21.9
Cobalt	28.4	31.1	28.4
Copper	26.4	10.2	7.90
Iron	10.3	1.67	1.57
Lead	25.1	8.55	6.03
Manganese	40.5	12.3	13.0
Mercury	ND	ND	ND
Molybdenum	21.6	20.1	19.2
Nickel ^a	29.8	20.4	18.2
Potassium	18.6	3.04	2.57
Rubidium	29.8	16.2	18.9
Selenium	ND	20.2	19.5
Silver ^a	31.9	31.0	29.2
Strontium	15.2	3.38	3.98
Thallium	39.0	16.0	19.5
Thorium	NR	NR	NR
Tin	ND	14.1	15.3
Titanium	13.3	4.15	3.74
Vanadium	NR	NR	NR
Zinc	26.6	13.3	11.1
Zirconium	20.2	5.63	5.18

Source: Reference 4

^a These values may be biased high because the concentration of these analytes in the soil samples was near the detection limit.

ND Not detected.

NR Not reported.

**TABLE 7
ACCURACY**

Analyte	Instrument															
	TN 9000				TN Lead Analyzer				X-MET 920 (SiLi Detector)				XL Spectrum Analyzer			
	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD
Sb	2	100-149	124.3	NA	--	--	--	--	--	--	--	--	--	--	--	--
As	5	68-115	92.8	17.3	5	44-105	83.4	23.2	4	9.7-91	47.7	39.7	5	38-535	189.8	206
Ba	9	98-198	135.3	36.9	--	--	--	--	9	18-848	168.2	262	--	--	--	--
Cd	2	99-129	114.3	NA	--	--	--	--	6	81-202	110.5	45.7	--	--	--	--
Cr	2	99-178	138.4	NA	--	--	--	--	7	22-273	143.1	93.8	3	98-625	279.2	300
Cu	8	61-140	95.0	28.8	6	38-107	79.1	27.0	11	10-210	111.8	72.1	8	95-480	203.0	147
Fe	6	78-155	103.7	26.1	6	89-159	102.3	28.6	6	48-94	80.4	16.2	6	26-187	108.6	52.9
Pb	11	66-138	98.9	19.2	11	68-131	97.4	18.4	12	23-94	72.7	20.9	13	80-234	107.3	39.9
Mn	4	81-104	93.1	9.70	3	92-152	113.1	33.8	--	--	--	--	--	--	--	--
Ni	3	99-122	109.8	12.0	--	--	--	--	--	--	--	--	3	57-123	87.5	33.5
Sr	8	110-178	132.6	23.8	--	--	--	--	--	--	--	--	7	86-209	125.1	39.5
Zn	11	41-130	94.3	24.0	10	81-133	100.0	19.7	12	46-181	106.6	34.7	11	31-199	94.6	42.5

Source: Reference 4

n Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
SD Standard deviation.
NA Not applicable; only two data points, therefore, a SD was not calculated.
%Rec. Percent recovery.
-- No data.

TABLE 8
ACCURACY FOR TN 9000^a

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.
RTC CRM-021	24.8	ND	NA	586	1135	193.5	4792	2908	60.7	144742	149947	103.6	546	224	40.9
RTC CRM-020	397	429	92.5	22.3	ND	NA	753	583	77.4	5195	3444	66.3	3022	3916	129.6
BCR CRM 143R	--	--	--	--	--	--	131	105	80.5	180	206	114.8	1055	1043	99.0
BCR CRM 141	--	--	--	--	--	--	32.6	ND	NA	29.4	ND	NA	81.3	ND	NA
USGS GXR-2	25.0	ND	NA	2240	2946	131.5	76.0	106	140.2	690	742	107.6	530	596	112.4
USGS GXR-6	330	294	88.9	1300	2581	198.5	66.0	ND	NA	101	80.9	80.1	118	ND	NA
NIST 2711	105	104	99.3	726	801	110.3	114	ND	NA	1162	1172	100.9	350	333	94.9
NIST 2710	626	722	115.4	707	782	110.6	2950	2834	96.1	5532	5420	98.0	6952	6476	93.2
NIST 2709	17.7	ND	NA	968	950	98.1	34.6	ND	NA	18.9	ND	NA	106	98.5	93.0
NIST 2704	23.4	ND	NA	414	443	107.0	98.6	105	106.2	161	167	103.5	438	427	97.4
CNRC PACS-1	211	143	67.7	--	772	NA	452	302	66.9	404	332	82.3	824	611	74.2
SARM-51	--	--	--	335	466	139.1	268	373	139.2	5200	7199	138.4	2200	2676	121.6
SARM-52	--	--	--	410	527	128.5	219	193	88.1	1200	1107	92.2	264	215	81.4

Source: Reference 4

^a All concentrations in milligrams per kilogram.
 %Rec. Percent recovery.
 ND Not detected.
 NA Not applicable.
 -- No data.

TABLE 9
REGRESSION PARAMETERS FOR COMPARABILITY¹

	Arsenic				Barium				Copper			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	824	0.94	1.62	0.94	1255	0.71	60.3	0.54	984	0.93	2.19	0.93
Soil 1	368	0.96	1.41	0.95	393	0.05	42.6	0.11	385	0.94	1.26	0.99
Soil 2	453	0.94	1.51	0.96	462	0.56	30.2	0.66	463	0.92	2.09	0.95
Soil 3	—	—	—	—	400	0.85	44.7	0.59	136	0.46	16.60	0.57
Prep 1	207	0.87	2.69	0.85	312	0.64	53.7	0.55	256	0.87	3.89	0.87
Prep 2	208	0.97	1.38	0.95	315	0.67	64.6	0.52	246	0.96	2.04	0.93
Prep 3	204	0.96	1.20	0.99	315	0.78	64.6	0.53	236	0.97	1.45	0.99
Prep 4	205	0.96	1.45	0.98	313	0.81	58.9	0.55	246	0.96	1.99	0.96

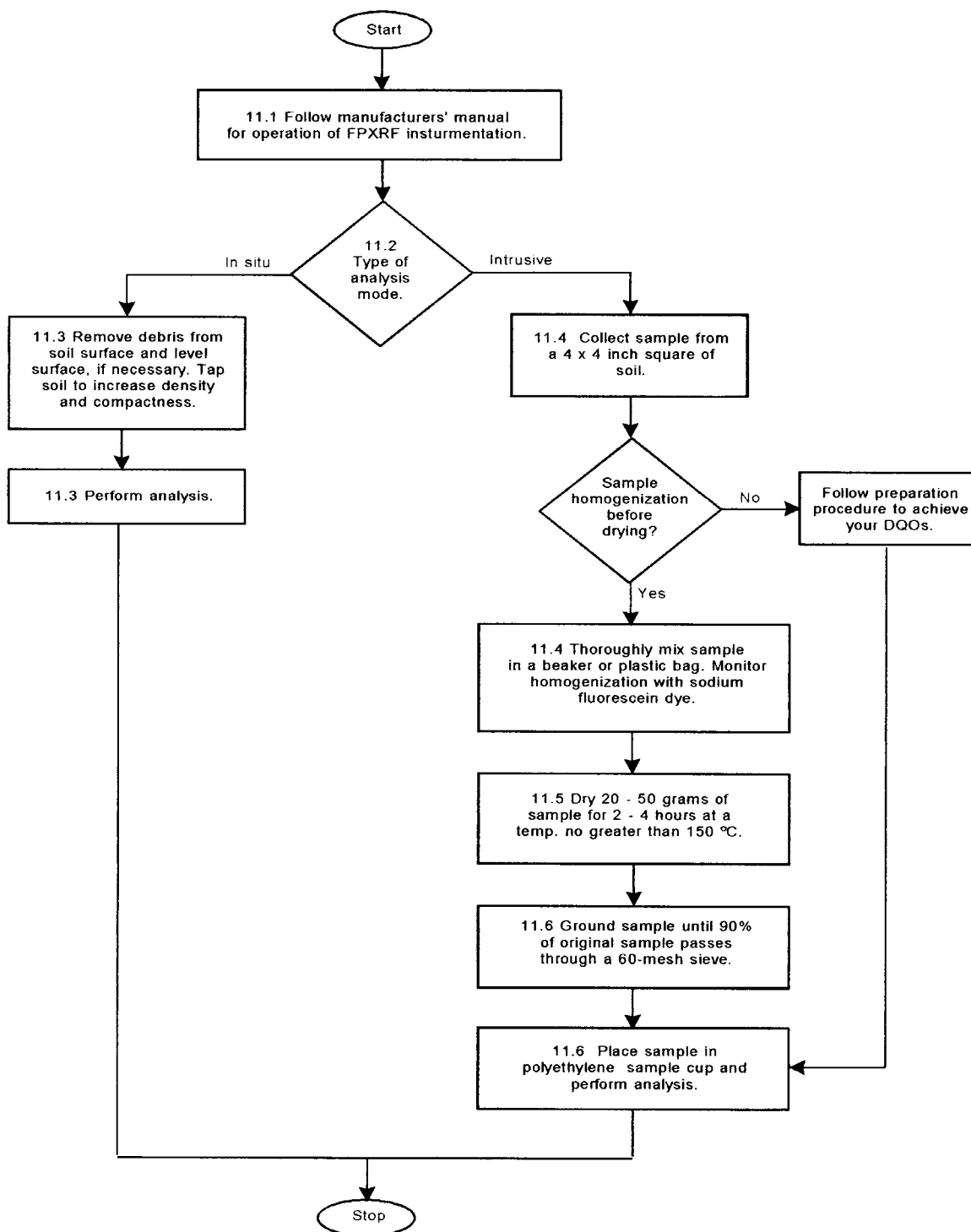
	Lead				Zinc				Chromium			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186	0.66	38.9	0.50
Prep 1	305	0.80	2.88	0.86	286	0.79	3.16	0.87	105	0.80	66.1	0.43
Prep 2	298	0.97	1.41	0.96	272	0.95	1.86	0.93	77	0.51	81.3	0.36
Prep 3	302	0.98	1.26	0.99	274	0.93	1.32	1.00	49	0.73	53.7	0.45
Prep 4	300	0.96	1.38	1.00	271	0.94	1.41	1.01	49	0.75	31.6	0.56

Source: Reference 4

- ¹ Log-transformed data
n Number of data points
r² Coefficient of determination
Int. Y-intercept
— No applicable data

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT



Appendix B

Determination of Sample Size

**APPENDIX B
SAMPLE SIZE DETERMINATION**

**STSIU IRAWP
CHINO MINES COMPANY - HURLEY, NM**

Parameter	Value	Description	Note
A	5%	False positive rate, gives 95% confidence.	5% chance of concluding area is clean when it is really still contaminated
B	20%	False negative rate	80% chance of concluding area is clean when it really is clean.
P ₀	5%	Target percentage goal.	Conclude area is clean if less than 5% of samples exceed 2,700 ppm.
P ₁	2.5%	Assumed achieved percentage.	Assumed percent of samples exceeding goal of 2,700 ppm achieved after excavation.
n _d ¹	384	Number of samples required.	Calculated value.

NOTES:

¹ Calculated using Equation 7.1 From EPA Guidance Document: Methods for Evaluating the Attainment of Cleanup Standards. Volume 1. EPA 1989 as shown below.

$$n_d = \left\{ \frac{Z_{1-B} \sqrt{P_1(1-P_1)} + Z_{1-A} \sqrt{P_0(1-P_0)}}{P_0 - P_1} \right\}^2$$

Appendix C

Standard Operating Procedures

STANDARD OPERATING PROCEDURE NO. 1

FIELD DOCUMENT CONTROL

Information relevant to field operations must be recorded in various forms, including logbooks, photographs, chain-of-custody records and field sample data sheets. Field document control procedures will be implemented to ensure that documents are trackable and accounted for when the project is completed.

Field Documents Subject to Control:

1. Project logbooks;
2. Field logbooks;
3. Field sample data sheets;
4. Chain-of-custody records;
5. Sample logbooks; and
6. Photographs, drawings, and annotated maps used during field activities.

Sample Numbering Scheme

CMC's AOC Data Administrator will assign a block of sample numbers on a project-by-project basis to those required to complete any type of sampling for AOC work. These sample numbers will be used for all samples prepared in the field, including QA/QC samples. The following sample numbering scheme for aqueous and non-aqueous samples will be used:

Uxx-NNNN

Where "xx" represents each investigation unit as follows:

- Lampbright Draw - 01;
- Hanover Creek Channel - 02;
- Whitewater Creek Channel - 03;
- Smelter - 04;
- Hurley Soils - 05;
- Tailing Affected Soils - 06;

- Ecological - 07; and
- Miscellaneous -08.

NNNN represents a four-character numeric string assigned as follows:

Background Report Sampling	See Note Below
Remedial Investigation	0001 through 1000
Remedial Investigation	1100 through 2000
Feasibility Study	2500 through 3000
Remedial Design	3100 through 4000
Remedial Action (RA)	4100 through 5000
Post RA Monitoring	5100 through 6000

Note: The Background Report sample numbers consist of combinations of numbers which will not be duplicated using the blocks of numbers specified above.

Additional blocks of sample numbers can be developed as the need arises and this SOP will be updated in such cases.

Each consultant will maintain a logbook defining field activities (SOP-2). The logbook entries will be named after the specific site and project to be performed. Documents created to collect data or information should have the date and signature of the personnel who are responsible for the measurements or observations recorded.

When field forms or logbooks are completed, original versions will be provided to the CMC AOC Data Administrator in Hurley, N.M. for placement in the master field document control section of the master project file. Records of sample bottle certification will be kept with the field logbook for filing in the master project file.

STANDARD OPERATING PROCEDURE NO. 2

FIELD LOGBOOK

A separate field logbook shall be used for each field task. Each logbook shall have a unique document control number. The logbooks shall be bound and have consecutively numbered pages. The information recorded in these logbooks shall be written in indelible ink. Entries shall be initialed and dated at the end of each day by the author, and a line drawn through the remainder of the page. Pages shall be consecutively numbered. Corrections to logbook entries shall consist of a single line-out deletion in indelible ink followed by the author's initials and the date. No field logbooks shall be destroyed or thrown away, even if they are illegible or contain inaccuracies that require replacement or correction. These logbooks or data forms, at a minimum, shall include the following entries:

- Purpose and description of proposed field task;
- Time and date fieldwork started;
- Location and description of work area and, if possible, map reference and photographs and sketches of well construction details, soils, pits, etc.;
- Names and titles of field personnel;
- Name and address of any field contacts;
- Meteorological conditions at the initiation of fieldwork and any ensuing changes in these conditions;
- Details of the fieldwork performed, with special attention to any deviations from the Field Sampling Plan (FSP) or Standard Operating Procedures (SOPs);
- All field measurements made;
- Level of personnel protective equipment;
- Field instrument calibration data;
- Field laboratory analytical results; and
- Personnel and equipment decontamination procedures.

For field sampling work, at a minimum, the following entries should be made:

- Sample location and number;
- Sample type (e.g., groundwater) and amount collected;

- Date and time of sample collection;
- Split samples taken by other parties. Note the type of sample, sample location, time/date, name of person, person's company, and any other pertinent information;
- Sampling method, particularly any deviations from the SOP;
- Suspected waste composition, including an estimate of the hazard level as being low or medium;
- Documentation or reference of preparation procedures for reagents or supplies that will become an integral part of the sample (e.g., filters and preserving reagents); and
- Sample preservation, handling, packaging, labeling, shipping information (e.g., weight), the shipping agent, and the laboratory that will receive the samples.

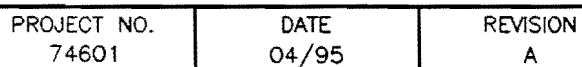
PHOTOGRAPHS

Photographs shall be taken of field activities using a camera-lens system with a perspective similar to the naked eye. Photographs should include a measured scale in the picture, when practical. The following items shall be recorded in the field logbook for each photograph taken:

- The photographer's name, the date, the time of the photograph, and the general direction faced;
- A brief description of the subject and the fieldwork portrayed in the picture; and
- Roll number and sequential number containing the photograph.

The slides or prints and associated negatives shall be placed in the master project files in CMC's office following development of the film. Supporting documentation from the field logbooks shall also be photocopied and placed in the master project files to accompany the particular slides or prints. Figure 2-1 presents an example of a photograph label. These photograph labels are intended to be attached to the individual photo placed in the master project file.

PHOTOGRAPH NUMBER: _____
DATE: _____
TIME: _____
DIRECTION: _____
PHOTOGRAPHER: _____
DESCRIPTION: _____



PHOTOGRAPH LABEL

STANDARD OPERATING PROCEDURE NO. 3

FIELD QUALITY CONTROL

Field Quality Control (QC) is a part of the project Quality Assurance/Quality Control program. This Standard Operating Procedure (SOP) describes the preparation and recommended collection frequency of various field QC samples for aqueous and soil/sediment media. Table 3.1 lists the QC sample types, preparation methods, and recommended frequencies for the field sampling program.

At least one set of field QC samples shall be prepared for each sampling event. An event is defined by any of the following conditions:

1. An initiation of a new sampling round; or
2. A significant change in sample type or media.

If the number of field QC samples taken is not equal to an integer multiple of the interval specified in Table 3.1, then the next highest multiple shall be used. For example, if a frequency of 1 in 20 is indicated and 28 samples are taken, then two field QC samples shall be prepared.

All field QC samples shall be labeled and shipped with field samples to the laboratory according to SOP-5. Sample custody shall be maintained using the procedures described in SOP-4.

Description of Field QC Measures

Field QC measures shall be implemented during sample collection activities to preserve sample integrity. Sampling equipment shall be decontaminated according to the appropriate SOPs to minimize potential cross-contamination. In addition, new surgical type gloves shall be donned at each sample location and, when possible, the sampling program shall proceed from "clean" to "dirty" areas.

Description of Field QC Samples

General descriptions of potentially applicable field QC samples follow below. The sample collection frequency shall be established by the site-specific Field Sampling Plan.

Blind Decon Rinseate Blank (BDRB) - A BDRB is a sample bottle containing distilled/deionized (DS/DI) water and preservative and is prepared at the sample site. A BDRB is prepared for dissolved metals by processing a representative amount of DS/DI water through the decontaminated sample collection container and filtering apparatus (if appropriate) and adding the appropriate preservative. A BDRB is prepared by processing a representative amount of DS/DI water through the decontaminated sample collection container only and adding the appropriate preservative. The appropriate sample number shall be written on the sample label, and the label shall be placed on the bottle.

Field External Contamination Blank (FECB) - A FECB is a sample bottle containing DS/DI water that is "sampled" through an unused filter and is prepared at the sample site. A FECB is prepared by processing a representative amount of DS/DI water through the decontaminated filtering apparatus (if appropriate) using a clean, unused filter. The appropriate sample number shall be written on the sample label, and the label shall be placed on the bottle. The sampler shall record the filter name and lot number in the field logbook.

Blind Bottle Blank (BBB) - A BBB is a sample bottle containing DS/DI water and preservatives and is prepared in the field laboratory. A BBB is contained in a sample bottle randomly chosen from the lot of bottles received from the supplier. A BBB is prepared by the same protocols as a normal sample but is not exposed to any "field conditions" or sampling equipment. The appropriate sample number shall be written on the sample label, and the label shall be placed on the bottle.

Blind Field Duplicate (BFD) - A BFD consists of split samples taken at the same location and time but placed in different sample containers for separate analysis. Each duplicate shall be analyzed for identical chemical parameters. A BFD is prepared as follows:

1. Collect an adequate volume of sample to accommodate two sample containers;
2. Process the samples as per SOP-16, SOP-21, or SOP-22 for each duplicate;
3. Label the two sample containers with appropriate sample numbers; and
4. Record duplicate number, sample number, and sample location in the field book.

The chain of custody documentation for the BFD should reflect an arbitrary sampling time, which is consistent with the sample set.

Trip Blank (TB) Sample - A TB sample is only required when volatile organic analyses are requested. The TB sample is prepared by the laboratory and consists of a sample bottle filled with Type II reagent water, transported to the site, handled like a sample and returned unopened to the laboratory for analysis. One trip blank per day shall be prepared and shipped with samples taken that day (see SOP-4).

REFERENCES

APHA, AWWA, and WPCF, 1985. Standard methods for the examination of water and wastewater, 16th Ed. M.H. Franson (ed). American Public Health Association, American Water Works Association, and Water Pollution Control Federation, Washington, D.C.

TABLE 3.1
RECOMMENDED FIELD QUALITY CONTROL SAMPLING PROGRAM

Quality Control Sample Name	Abbreviation	Applicable Sample Media	Preparation Location	Recommended Collection Frequency
Blind Decon Rinseate Blanks	BDRB	Aqueous Soil/Sediment	Sample Site	Once per 20 or Once per Sampling Event
Field External Contamination Blank	FECB	Aqueous	Sample Site	Once per Day per Matrix
Blind Bottle Blank ^a	BBB	Aqueous	Field Lab. Retained in Lab	Once per 20 or Once per Sampling Event
Blind Field Duplicates	BFD	Aqueous Soil/Sediment	Sample Site	Once per 10 or Once per Week
Trip Blank	TB	Aqueous (VOCs Only)	Laboratory	Once per Day

Note:

- a. This QC sample is not required if pre-cleaned sample containers and certification are supplied by the analytical laboratory.

STANDARD OPERATING PROCEDURE NO. 4

SAMPLE CUSTODY AND DOCUMENTATION PROCEDURES

A stringent, established program of sample chain-of-custody procedures shall be followed during field sample collection and handling activities and transfer of the samples to the analytical laboratory. Whenever possible, preprinted labels should be used to ensure that all necessary information is retained with the sample. Shipping manifests shall be utilized to maintain control over access to the destination of samples after shipment from the sample collection site.

Figures 4-1, 4-2, 4-3, 4-4 and 4-5 (A and B) show examples of the sample label, field sample data sheet, chain-of-custody record, field sample data sheet for surface water and soil sampling data sheets, respectively. The use of each form is discussed below.

Sample Label

Each sample shall be labeled, and the following information recorded on the label:

1. Project number;
2. Laboratory analyses;
3. Sample type (grab or composite, media sampled);
4. Sample identification (well number for groundwater samples; soil boring number, sample number, and sample depth for soil samples, etc.);
5. Date and time sample was taken;
6. Sampler's name;
7. Sample ID number (in accordance with SOP-1, a unique serial number stamped or written on each sample label);
8. Preservative added; and
9. Remarks, including pertinent field observations.

Field Sample Data Sheet

The field sample data sheet is completed in the field and signed by the individual physically in charge of sample collection. The field sample data sheet correlates the assigned sample bottle designation to a specific well or sample location or other distinguishing feature or attribute (e.g., blank sample, replicate sample, purge evaluation sample, etc.)

Chain-of-Custody Record

Chain-of-custody (COC) records ensure that samples are traceable from the time of collection until they are received and analyzed by the analytical laboratory. The COC shall be sealed in the sample shipping container. The shipping agent or courier is not required to sign the COC. Upon arrival at the lab, the sample custodian checks the custody seals on the sample shipping container, opens the container and signs as receiving the sample and noting the condition of the custody seal (e.g., intact).


A sample is in a person's custody if one of the following criteria is met:

1. It is in the person's possession;
2. It is in the person's view after being in possession;
3. It has been locked up to prevent tampering after it was in the person's possession; or
4. It was in the person's possession and was then transferred to a designated secure area.

The COC record is completed and signed in the field by the individual physically in charge of its custody. The COC record should be completed concurrently with the field sample data sheet. The sampler is personally responsible for the care and custody of the sample until it is shipped.

When transferring possession of the samples, the individuals relinquishing and receiving the sample shall sign, date, and write the time of day on the COC record. Samples in separate coolers shall not be included in the same COC record. The COC record is enclosed with the samples in each given cooler after it has been signed by the sampler.

The COC record also serves as the laboratory request form. As shown on Figure 4-3, a space is included on the form to list the analyses requested for each sample.

		INORGANIC (Unpreserved)	
Phone (208) 784-1258 One Government Gulch • Kellogg, ID 83837			
CLIENT: _____			
LOCATION: _____			
SAMPLE ID: _____		# _____	OF _____
DATE: _____	TIME: _____	A.M. P.M.	BY: _____
<input type="checkbox"/> FILTERED		<input type="checkbox"/> UNFILTERED	
ANALYSES: _____			

LABEL COLOR IDENTIFICATION

Inorganics	-	white
Organics	-	blue
Metals	-	red



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FIGURE 4-1

SAMPLE LABEL

STEFFEN ROBERTSON AND KIRSTEN

Field Sample Data

PROJECT No. _____
PAGE ____ OF _____

PROJECT NAME _____ SAMPLED BY _____
STATION NO./LOCATION _____ DATE _____

SKETCH ON BACK ☐ YES ☐ NO PHOTOGRAPHS ☐ YES ☐ NO ROLL NO./EXPOSURE NO. _____

FIELD DATA

TIME _____ AIR TEMP. °F _____ WEATHER _____

WELL DEPTH _____ WATER DEPTH _____ SAMPLE DEPTH _____ SAMPLE METHOD _____

VOL. PURGED _____ SAMPLE TEMP. _____ °C ☐ IN SITU ☐ IN BOTTLE SP. COND. _____ / _____ AT 25°C ☐ IN SITU ☐ IN BOTTLE

pH _____ ☐ IN SITU ☐ IN BOTTLE Eh _____ ☐ IN SITU ☐ IN BOTTLE DISSOLVED O₂ _____ ppm ☐ IN SITU ☐ IN BOTTLE

BOTTLE ID	LAB ID	VOL	MATERIAL	FILTERED	PRES./VOL.	ANALYSIS REQUESTED

FIELD PARAMETERS:

_____ GALLON pH - _____ EH - _____ TEMP. _____
_____ GALLON pH - _____ EH - _____ TEMP. _____
_____ GALLON pH - _____ EH - _____ TEMP. _____

REMARKS: _____

FIELD EQUIPMENT QUALITY ASSURANCE CHECKLIST

pH METER BUFFER CHECK pH 4 _____ pH 7 _____ pH 10 _____
SP. COND. METER STANDARDS CHECK _____ Eh PROBE _____
PUMP TUBING RINSED _____ CHANGED _____ SAMPLER BLANK _____
FILTRATION BLANK WITH PRES. _____ FILTERS ACID WASHED _____
SAMPLER'S SIGNATURE _____

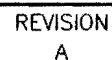
Page _____ of _____

Phone Number:

3) Ship samples promptly following collection.

1 = Surface Water, 2 = Ground Water
3 = Soil/Sediment, 4 = Rinsate, 5 = Oil
6 = Waste, 7 = Other (Specify)

SVL JOB #

SVL-COC 5/93

SAMPLE CHAIN OF
CUSTODY RECORD

PROJECT No. _____
PAGE __ OF _____

PROJECT NAME _____ SAMPLED BY _____
STATION NO./LOCATION _____ DATE _____

SKETCH ON BACK ☐ YES ☐ NO PHOTOGRAPHS ☐ YES ☐ NO ROLL NO./EXPOSURE NO. _____

FIELD DATA

TIME _____ AIR TEMP. °F _____ WEATHER _____

TYPE: STREAM ☐ POND ☐ OTHER ☐ SAMPLE DEPTH _____ STREAM WIDTH _____ FLOW VELOCITY _____
NAME _____

DISTANCE FROM BANK _____ SAMPLE DEPTH _____ SAMPLE TEMP _____ ☐ IN SITU ☐ IN BOTTLE SP. COND. _____ / _____ 25°C ☐ IN SITU ☐ IN BOTT

pH _____ ☐ IN SITU ☐ IN BOTTLE Eh _____ ☐ IN SITU ☐ IN BOTTLE DISSOLVED O₂ _____ ppm ☐ IN SITU ☐ IN BOTT

BOTTLE ID	LAB ID	VOL	MATERIAL	FILTERED	PRES./VOL.	ANALYSIS REQUESTED

REMARKS: _____

FIELD EQUIPMENT QUALITY ASSURANCE CHECKLIST

pH METER BUFFER CHECK pH 4 _____ pH 7 _____ pH 10 _____
SP. COND. METER STANDARDS CHECK _____ Eh PROBE _____
PUMP TUBING RINSED _____ CHANGED _____ SAMPLER BLANK _____
FILTRATION BLANK WITH PRES. _____ FILTERS ACID WASHED _____
SAMPLER'S SIGNATURE _____

**SURFACE SOIL DATA
COLLECTION FORM**

Sample Number _____
Collection Date _____
Collection Time _____
Location Code _____
Chain of Custody No. _____

Coordinates North or Y _____ East of X _____

Sample Location _____

Composite (Y/N) _____

Composite Description _____

Collection Method _____

Sample Team Leader _____

Sample Team Member _____

Sample Team Member _____

Sample Team Member _____

Container Size (OZ) _____ % Full _____

Comments _____

Completed By: _____

Print Name

Signature

Date

Subcontractor: _____

FIGURE 4-5A

**SURFACE SOIL SAMPLING
FIELD ACTIVITIES REPORT FORM**

Project Name _____

Site Identification _____ Date _____

Sampler _____

SAMPLE POINT	GRID LOCATION	TIME	COMMENT

Completed By: _____
Print name Signature Date

Subcontractor: _____

FIGURE 4-5B

STANDARD OPERATING PROCEDURE NO. 5 PACKAGING AND SHIPPING OF ENVIRONMENTAL SAMPLE CONTAINERS

Packaging of Sample Containers

1. Follow 40 CFR 261.1 (d) regulations for the shipment of samples, (copy attached).
2. Before packing the samples, check lids for tightness and tape them, if necessary. Do not use electrical tape or other tape with adhesive containing volatile organics if volatile organic sampling is requested.
3. Seal each sample container individually inside a single, 2-mil-thick (or thicker), zip-lock polyethylene bag. Position sample container so that the sample label can be read through the bag.
4. Place one or more bagged samples inside a strong shipping container, such as a metal picnic cooler or Department of Transportation (DOT)-approved fiberboard box, that has been lined with a large polyethylene bag. Surround all containers with non-combustible, cushioning material (e.g., vermiculite) to provide stability during transport. Use ice, Blue Ice or similar product for cooling the samples during shipment.
5. The chain-of-custody record and sample packing list shall be placed in an envelope and taped to the inside lid of the shipping container (DOT shipping papers are not required).
6. Close the shipping container and seal it with two or more custody seals placed across the container opening and tape the container shut using fiberglass tape (or equivalent). Be careful not to break the custody seals.

Marking/Labeling of Shipping Container

1. Clearly print in indelible ink the laboratory name and address and the return name and address in unabbreviated form on the shipping container.
2. Clearly print in indelible ink on top of the shipping container the following:
"Environmental Samples," and "This End Up." Draw upward arrows on all four sides of the container.

Note:

Holding time begins on the date and time of sample collection. Be sure to ship samples with enough lead time to meet these holding times. Whenever possible, notify the analytical laboratory before sample collection, by an appropriate method, to ensure that analysis requirements can be met.

If samples are stored by the sampler, the preservation techniques implemented by the sampler must be documented. Samples must remain secure under a valid chain of custody.

* STA.#2 * F:\CHINO\74601\SOP\FIGS-1.DWG * APR 20, 1995 * 1:22:47 PM *

CUSTODY SEAL

Person Collecting Sample _____ Sample No. _____
(signature)
Date Collected _____ Time Collected _____



PROJECT NO.
74601

DATE
04/95

REVISION
A

FIGURE 5-1

SAMPLE CUSTODY SEAL

ATTACHMENT TO SOP 5

40 CRF 261.1 (d)

REGULATIONS FOR SAMPLE SHIPMENT

Code of Federal Regulations
Title 40: Protection of the
Environment
Chapter I - Environmental Protection
Agency, Part 261.4(d)

(d) Samples. (1) Except as provided in paragraph (d)(2) of this section, a sample of solid waste or a sample of water, soil, or air, which is collected for the sole purpose of testing to determine its characteristics or composition, is not subject to any requirements of this part or Parts 262 through 268 or Part 270 or Part 124 of this chapter or to the notification requirements of section 3010 of RCRA, when:

- (i) The sample is being transported to a laboratory for the purpose of testing; or
- (ii) The sample is being transported back to the sample collector after testing; or
- (iii) The sample is being stored by the sample collector before transport to a laboratory for testing; or
- (iv) The sample is being stored in a laboratory before testing; or
- (v) The sample is being stored in a laboratory after testing but before it is returned to the sample collector; or
- (vi) The sample is being stored temporarily in the laboratory after testing for a specific purpose (for example, until conclusion of a court case or enforcement action where further testing of the sample may be necessary).

(2) In order to qualify for the exemption in paragraphs (d)(1) (i) and (ii) of this section, a sample collector shipping samples to a laboratory and a laboratory returning samples to a sample collector must:

(i) Comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

(ii) Comply with the following requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample:

(A) Assure that the following information accompanies the sample:

- (1) The sample collector's name, mailing address, and telephone number;
- (2) The laboratory's name, mailing address, and telephone number;
- (3) The quantity of the sample;
- (4) The date of shipment; and
- (5) A description of the sample.

(B) Package the sample so that it does not leak, spill, or vaporize from its packaging.

(3) This exemption does not apply if the laboratory determines that the waste is hazardous but the laboratory is no longer meeting any of the conditions stated in paragraph (d)(1) of this section.

**STANDARD OPERATING PROCEDURE NO. 6
DECONTAMINATION OF EQUIPMENT USED TO
SAMPLE SOIL AND WATER**

The field hydrogeologist or geologist shall set up the area used to decontaminate soil and water sampling equipment in the manner shown on Figure 6-1. This area shall be located approximately 15 feet away from the specific sampling area. The personnel performing the decontamination procedures shall wear disposable surgical gloves.

Procedures Used to Decontaminate Soil Sampling Equipment

The following decontamination procedure shall be utilized for inorganically contaminated soil sampling equipment. If the sample will not be analyzed for trace metals, the nitric acid wash may be skipped.

Table 6.1 lists the equipment that shall be used to decontaminate the soil sampling equipment. The specific procedures for decontaminating soil sampling equipment include:

1. At Station No. 1, first wash the contaminated equipment in a tub containing tap water to remove the soil material. Follow with a second wash in a tub containing water mixed with a phosphate-free industrial strength soap such as Alconox.
2. Move the equipment to the wash tub in Station No. 2. Rinse the equipment with clean water, wash with 0.1 normal nitric acid (HNO_3) and then with distilled/deionized (DS/DI) water.
3. At Station No. 3, place the clean equipment on plastic sheeting until it is used again. Soil sampling equipment that will not be used immediately shall be wrapped in clean plastic.

Procedures Used to Decontaminate Water Sampling Equipment

The following decontamination procedure shall be utilized for inorganically contaminated water sampling equipment. If the sample will not be analyzed for trace metals, the nitric acid wash may be skipped.

Table 6.2 lists the equipment that shall be used to decontaminate water sampling equipment (To decontaminate pumps, see the following Section).

The specific procedures for decontaminating water sampling equipment include:

1. At Station No. 1, wash the contaminated equipment in a tub containing water mixed with a phosphate-free industrial strength soap such as Alconox.
2. Move the equipment to the wash tub in Station No. 2. First, rinse the equipment with DS/DI water. Then rinse the equipment with dilute (0.1 normal) nitric acid and follow with a second rinse using DS/DI water.
3. At Station No. 3, place the clean equipment on plastic sheeting until it is used again. Water sampling equipment that will not be used immediately shall be wrapped in clean plastic.

Disposal of Decontamination Materials

Based on the sample data results from the RI Background Report, disposal of investigation-derived waste shall consist of the following:

1. Following the decontamination of all water sampling equipment, the disposable gloves and used plastic from Station No.3 shall be placed in garbage bags and disposed of in a trash collection facility.
2. The wash and rinse water from Station No.1 and No.2 shall be disposed of on the ground surface at the sample location.

Decontamination of Sampling Pumps

When samples are collected by sampling pumps, sampling shall begin with the well containing the lowest anticipated analyte concentration. Successive samples should be obtained from wells anticipated to have increasing analyte concentrations. Use of dedicated pump equipment is preferable when feasible. Table 6.3 lists the decontamination equipment required.

When pumps (e.g., submersible or bladder) are submerged below the water surface to collect water samples, they should be cleaned and flushed between uses. This cleaning process consists of an external detergent wash and high-pressure tap water rinse, or steam cleaning, of the pump casing, tubing, and cables, followed by a flush of potable water through the pump. This flushing can be accomplished by pouring clean tap water from a carboy into the end of the discharge tube and working it down to the inside of the pump. The procedure should be repeated; then the tubing and inside of the pump should be rinsed with DS/DI water. Alternatively, the sampling pump may be

flushed by pumping a volume of potable water equal to two times the total capacity of the pump. This may be followed by pumping the same volume of DS/DI through the pump.

Surface pumps (e.g., peristaltic or diaphragm) used for well evacuation shall be cleaned between well locations. However, a new length of polyethylene tubing must be used for each well and discarded after use. The pump and hose should always be placed on clean polyethylene sheeting to avoid contact with the ground surface.

TABLE 6.1
DECONTAMINATION EQUIPMENT FOR SOIL SAMPLING

Equipment List for Decontamination

<u>Item</u>	<u>Quantity</u>
3-gallon plastic tubs	3
5-gallon plastic container, tap water	a
5-gallon carboy, DS/DI water	a
Alconox	a
Hard-bristle brushes	2
Plastic sheeting or garbage bags	a
Latex gloves	a
Kimwipes	a
0.1 Normal Nitric Acid	a
55-gallon drum(s)	a
Spray Paint	a

Equipment at Decontamination Stations

Station No. 1

Alconox, tap water, two 3-gallon plastic washtubs, scrub brush, DS/DI water

Station No. 2

3-gallon plastic washtub, DS/DI water, 0.1 Normal nitric acid

Station No. 3

Plastic sheeting or garbage bag

Note:

- a. Quantity is dependent on the size of the sampling effort and is, therefore, left to the discretion of the field hydrogeologist or geologist.

TABLE 6.2
DECONTAMINATION EQUIPMENT FOR WATER SAMPLING

Equipment List for Decontamination

<u>Item</u>	<u>Quantity</u>
3-gallon plastic tubs	2
5-gallon plastic container, tap water	a
5-gallon carboy, DS/DI water	a
Alconox	a
Dilute (1 to 1) nitric acid ^b	a
Hard-bristle brushes	2
Plastic sheeting or garbage bags	a
Latex gloves	a
Kimwipes	a
0.1 Normal Nitric Acid	a
55-gallon drum(s)	a
Spray Paint	a

Equipment at Decontamination Stations

Station No. 1

Alconox, tap water, two 3-gallon plastic washtub, scrub brush, DS/DI water

Station No. 2

3-gallon plastic washtub, DS/DI water, dilute (1 to 1) nitric acid^b

Station No. 3

Plastic sheeting or garbage bag

Note:

- a. Quantity is dependent on the size of the sampling effort and is, therefore, left to the discretion of the field hydrogeologist or geologist.
- b. Mix equal volumes of concentrated nitric acid with DS/DI water.

TABLE 6.3
DECONTAMINATION EQUIPMENT FOR SAMPLING PUMPS
EQUIPMENT LIST FOR DECONTAMINATION OF SUBMERSIBLE PUMPS

Equipment List for Decontamination

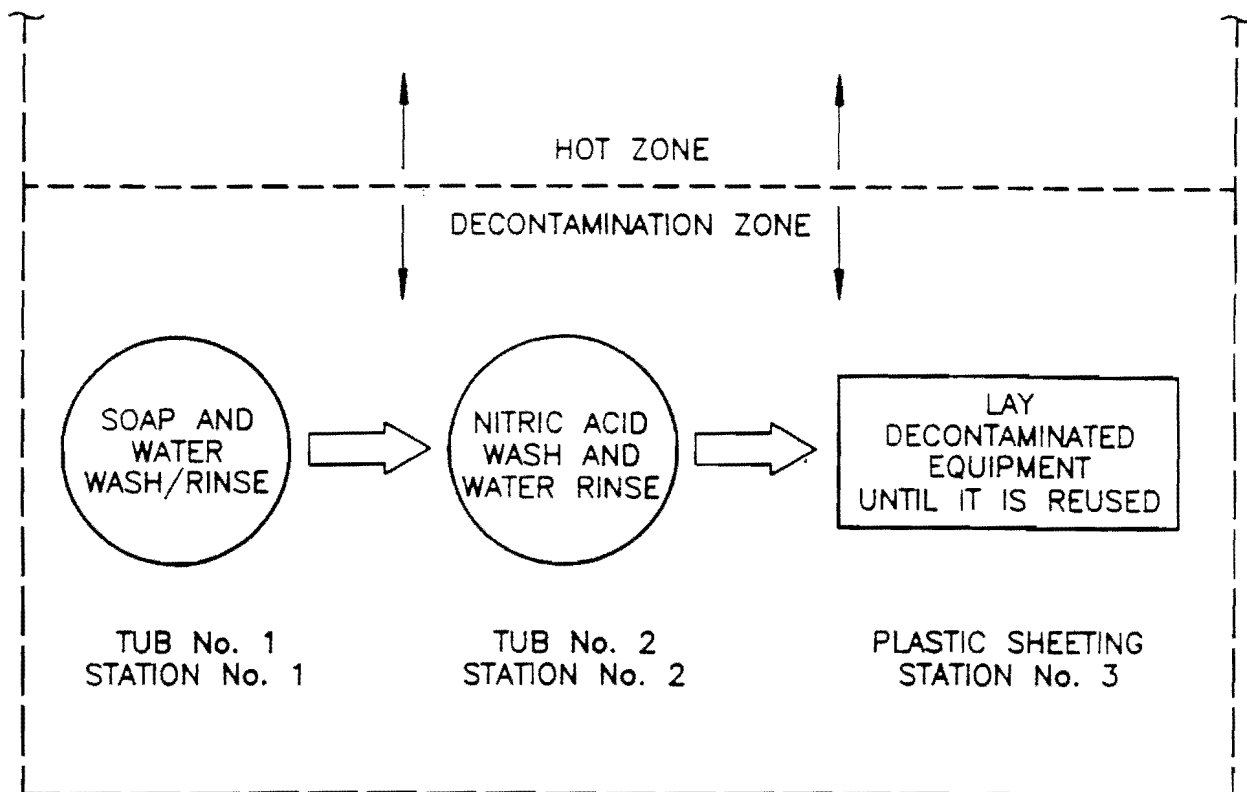
<u>Item</u>	<u>Quantity</u>
Alconox	a
Tap water	a
5-gallon carboy, DS/DI water	a
Hard-bristle brushes	1
Plastic sheeting or garbage bags	a
Personal protective equipment	a,b
30-gallon plastic trash can or plastic overpack drum	1
55-gallon drum(s)	a
Drum labels	a
Spray paint	a
Steam cleaner	optional

Equipment at Decontamination Stations

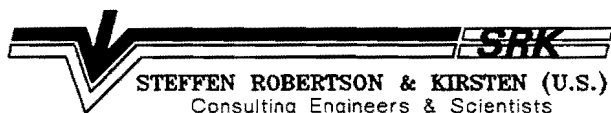
<u>Item</u>	<u>Quantity</u>
Polyethylene tubing	a
Plastic sheeting or garbage bags	a

Note:

- a. Quantity is dependent on the size of the sampling effort and is, therefore, left to the discretion of the field hydrogeologist or geologist.
- b. Type of protective equipment as specified in the site-specific Health and Safety Plan.



* STA.#2 * F:\CHINO\74601\SOP\Fig6-1.DWG * APR 20, 1995 * 1:15:39 PM *



PROJECT NO.
74601

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04/95

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FIGURE 6-1

TYPICAL DECONTAMINATION
STATIONS LAYOUT

STANDARD OPERATING PROCEDURE NO. 7
REQUESTING ENVIRONMENTAL LABORATORY SERVICES

The standardized form to be used for requesting environmental laboratory services from the contracted laboratories is presented. This form serves two main purposes: (1) to request bottles and other sampling materials for a planned sampling program and (2) to provide advance notification to the laboratory of future laboratory analyses requirements.

Request for
Environmental Laboratory Services

SOP No. 7
Revision 1
June 1996
Page 2 of 4

FAX
CHINO MINES COMPANY - AOC
REQUEST FOR ENVIRONMENTAL LABORATORY SERVICES

Date: _____

Fax to: _____

From: _____

Attention: _____

Phone: _____

Fax: _____

Ship to: _____

Attention: _____

Phone: _____

Fax: _____

Request for
Environmental Laboratory Services

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Analysis	Number of Samples		Remarks
	Water	Solid	
PHYSICAL/CHEMICAL			
pH			
Specific Conductance			
TOC			
TOX			
GENERAL INORGANIC CHEMISTRY			
Chloride			
Iron			
Manganese			
Sulfate			
Fluoride			
Nitrate/Nitrite			
GENERAL ORGANIC CHEMISTRY			
BTEX/MTBE			
Oil & Grease			
ORGANIC			
PCB			
Phenols			
Volatiles			
Semi-volatiles			
Pesticides/Herbicides			
RADIOCHEMISTRY (Specify)			
METALS - GRAPHITE FURNACE			
METALS - ICP or FLAME			
RCRA CHARACTERISTICS			
TCLP			
OTHER			

Request for
Environmental Laboratory Services

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Date Bottles Required: _____

Anticipated Date Samples to be Shipped for Analysis: _____

Special Instructions: _____

STANDARD OPERATING PROCEDURE NO. 14

SAMPLING, PRESERVATION AND CONTAINERIZATION

This Standard Operating Procedure (SOP) describes the techniques and quality control measures used to sample, prepare, and handle water subject to the analyses listed below. Tables 14.1 through 14.3 summarize the information in this SOP. In addition, Tables 14.1 and 14.3 summarize information for sampling, preservation and containerization of solid samples subject to specified analyses.

1. Acidity and Alkalinity;
2. Bicarbonate/Carbonate;
3. Chloride;
4. Fluoride;
5. Hardness;
6. Metals (Al, As, Ba, Cd, Ca, Co, Cr, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Ag, Na, Sr, Zn);
7. Nitrate;
8. Silica;
9. Semi-volatile Organic Compounds;
10. Solids {Total dissolved solids (TDS), total suspended solids (TSS)};
11. Sulfate;
12. Total Organic Carbon in Water; and
13. Volatile Organic Compounds.

All sample containers are assumed to be pre-cleaned by the laboratory prior to shipment to the site. If pre-cleaned sample containers are not available at the time of sampling, follow additional container preparation procedures below.

Acidity and Alkalinity

Apparatus and Materials

1. Polyethylene or borosilicate glass (pyrex or equivalent) bottles.

Sample Collection, Preservation and Handling:

1. Fill sample bottles completely, leaving no headspace, then cap tightly.

2. Store samples at 4 degrees Centigrade (°C)
3. All samples should be analyzed within 14 days of collection.

Quality Control:

1. Dissolved gases contributing to acidity or alkalinity, such as carbon dioxide, hydrogen sulfide, or ammonia, may be lost or gained during sampling or storage. To prevent this, sample bottles should be filled completely, leaving no headspace, then cap tightly.

Bicarbonate/Carbonate

Apparatus and Materials:

1. Polyethylene or glass bottles.

Sample Collection, Preservation, and Handling:

1. Completely fill the sample bottle, leaving no headspace, and cap tightly.
2. Store sample at 4°C until analyzed.
3. All samples should be analyzed within 14 days of collection.

Quality Control:

1. Carbon dioxide may be lost or gained during sampling and storage. To prevent this, sample bottles must be filled completely, leaving no headspace, then capped tightly.

Chloride

Apparatus and Materials:

1. Polyethylene or glass bottles.

Sample Collection, Preservation, and Handling:

1. All samples must be analyzed within 28 days of collection.

Quality Control:

1. No special precautions.

Fluoride

Apparatus and Materials:

1. Polyethylene bottles.

Samples Collection, Preservation, and Handling:

1. Polyethylene bottles are required for collecting and storing samples for fluoride analysis. Always rinse the bottle with a portion of the sample.
2. All samples must be analyzed within 28 days of collection.

Quality Control:

1. Sample bottle must be rinsed with a portion of the sample prior to collecting the sample.
2. Only polyethylene bottles may be used.

Hardness

Apparatus and Materials:

1. Polyethylene or glass bottles.
2. Dilute nitric acid (1 to 1): Mix equal volumes of concentrated nitric acid, HNO_3 , with distilled/deionized (DS/DI) water.

Sample Collection, Preservation, and Handling:

1. Acidify with HNO_3 to pH 2 or lower.
2. Samples should be analyzed within 6 months of collection.

Quality Control:

1. Errors may be introduced during sampling and storage by failure to remove residues of previous samples from the sample container; therefore, all containers and sampling equipment should be thoroughly cleaned before use.

Metals

Apparatus and Materials:

1. Polyethylene or glass bottles.
2. Dilute nitric acid (1 to 1): Mix equal volumes of concentrated nitric acid, HNO_3 , with distilled/deionized (DS/DI) water.
3. DS/DI water.

Sample Collection, Preservation, and Handling:

1. Wash and rinse sample container thoroughly with dilute nitric acid (1 to 1), then with DS/DI water before use.
2. Acidify sample with dilute nitric acid (1 to 1) to a pH of 2 or less. Normally, 3 milliliters (ml) of dilute nitric acid per liter should be sufficient to preserve each sample. This will keep the metals in solution and minimize their adsorption on the container wall. Preservatives should be added sparingly to meet the requirements for the analytical method. The sample pH should be re-checked after a short time to ensure that the acid has not been buffered out of the sample.

3. All samples should be analyzed within 6 months of collection. An exception is mercury analysis, which must be completed within 28 days.
4. Samples filtered for dissolved metals analysis should be preserved after filtration rather than prior to filtration.

Quality Control:

1. Serious errors may be introduced during sampling and storage by failure to remove residues of previous samples from the sample container; therefore, follow the described rinsing procedure for all containers and sampling equipment.

Nitrate

Apparatus and Materials:

1. Polyethylene or glass bottles.

Sample Collection, Preservation, and Handling:

1. Store samples at 4°C.
2. All samples should be analyzed within 48 hours of collection.

Quality Control:

1. Nitrate determinations should be made promptly after sampling.

Semi-volatile Organic Compounds

Apparatus and Materials:

1. Threaded amber glass bottles, 1-liter size, French or Boston Round design or equivalent is required.
2. Bottle caps - threaded, screw on, and lined with Teflon.

Sample Collection, Preservation, and Handling

1. Bottles must not be pre-rinsed with sample before collection.
2. Fill bottle approximately 90% full, leaving headspace, then cap tightly.

Quality Control:

1. Sample must be maintained at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and protected from light.
2. Extract within 7 days of collection (aqueous samples) or 14 days (solid samples), analyze within 40 days of extraction.

Silica

Apparatus and Materials:

1. Polyethylene bottles.

Sample Collection, Preservation, and Handling:

1. Collect samples in bottles of polyethylene plastic only; do not use glassware for any sample handling.
2. Store samples at 4°C .
3. All samples must be analyzed within 28 days of collection.

Quality Control:

1. If samples are stored in glass, silica may leach into the sample and raise concentrations; therefore, glassware cannot be used.

Solids (TDS, TSS)

Apparatus and Materials:

1. Polyethylene or glass bottles.

Sample Collection, Preservation, and Handling:

1. Store samples at 4°C.
2. Samples must be analyzed within seven days following collection,

Quality Control:

1. Sample should be analyzed as soon as possible after collection for best results.
2. Exclude unrepresentative particles such as leaves, sticks, or large solids.
3. Glass bottles are desirable. Plastic bottles are satisfactory provided that the material in suspension in the sample does not adhere to the walls of the container. Store samples that are likely to contain iron or manganese so that oxygen will not come into contact with the water. Analyze these samples promptly to minimize the possibility of chemical or physical change during storage.

Sulfate

Apparatus and Materials:

1. Polyethylene or glass bottles.

Sample Collection, Preservation, and Handling:

1. Store samples at 4°C.
2. All samples must be analyzed within 28 days of collection.

Quality Control:

1. In the presence of organic matter, certain bacteria may reduce sulfate to sulfide. To avoid this, samples should be stored at or below 4°C.

Total Organic Carbon in Water

Apparatus and Materials:

1. Amber glass or polyethylene bottles, with Teflon-lined caps.
2. Concentrated, reagent-grade, sulfuric acid (H_2SO_4) or hydrochloric acid (HCL).

Sample Collection, Preservation, and Handling:

1. Acidify samples with concentrated sulfuric acid or hydrochloric acid to a pH of 2 or less.
2. Fill bottle completely, leaving no headspace, then cap tightly.
3. Store samples at 4°C.
4. All samples should be analyzed within 28 days of collection.

Quality Control:

1. Avoid exposure of the sample to light and atmosphere; minimize storage time.

Volatile Organic Compounds

Apparatus and Materials:

1. Forty-ml amber glass vials with Teflon-faced, silicon screw caps.

Sample Collection, Preservation, and Handling:

1. Use two bottles per sample.
2. Completely fill sample vial, leaving no headspace, then cap tightly.
3. Sample must be maintained at 4°C, and protected from light.
4. Preserve sample with HCl, (pH of 2 or less), to minimize degradation by microbial action.

Quality Control:

1. Sample vials must be filled completely, leaving no headspace, and capped tightly.
2. Unpreserved VOC samples must be analyzed within 7 days of sample collection.
3. Do not use electrical tape or other tape with adhesive containing volatile organics such as toluene.

TABLE 14.1
RECOMMENDED SAMPLING AND PRESERVATION PROCEDURES

Parameter	Collection Technique	Container^a	Preservation	Holding Time^b	Minimum Required Volume (ml)
Acidity	Grab or composite	P, G	Cool, 4°C	14 days	100
Alkalinity	Grab or composite	P, G	Cool, 4°C	14 days	100
Bicarbonate	Grab only	P, G	Cool, 4°C	14 days	100
Carbonate	Grab only	P, G	Cool, 4°C	14 days	100
Chloride	Grab or composite	P, G	None required	28 days	50
Fluoride	Grab or composite	P	None required	28 days	300
Hardness	Grab or composite	P, G	HNO ₃ to pH<2	6 months	100

TABLE 14.1
RECOMMENDED SAMPLING AND PRESERVATION PROCEDURES

Parameter	Collection Technique	Container^a	Preservation	Holding Time^b	Minimum Required Volume (ml)
METALS					
Dissolved	Grab or composite	P, G	Filter on-site, HNO ₃ to pH<2	6 months, except Hg - 28 days	200
Suspended	Grab or composite	P, G	Filter on-site	6 months, except Hg - 28 days	200
Total	Grab or composite	P, G	HNO ₃ to pH <2	6 months, except Hg - 28 days	100
Nitrate	Grab or composite	P, G	Cool, 4°C,	48 hours	100
Semi-volatile Organic Compounds	Grab or composite	G, Teflon-lined cap	Cool, 4°C No preservative	7 days to extract 40 days to analysis	1,000

TABLE 14.1
RECOMMENDED SAMPLING AND PRESERVATION PROCEDURES

Parameter	Collection Technique	Container^a	Preservation	Holding Time^b	Minimum Required Volume (ml)
Silica	Grab or composite	P	Cool, 4°C	28 days	50
SOLIDS					
Dissolved (non-filterable)	Grab or composite	P, G	Cool, 4°C	7 days	100
Suspended (filterable)	Grab or composite	P, G	Cool, 4°C	7 days	100
Sulfate	Grab or composite	P, G	Cool, 4°C	28 days	50

TABLE 14.1
RECOMMENDED SAMPLING AND PRESERVATION PROCEDURES

Parameter	Collection Technique	Container^a	Preservation	Holding Time^b	Minimum Required Volume (ml)
TOC	Grab or composite	P,G, Teflon-lined cap	Cool, 4°C H ₂ SO ₄ or HCL to pH<2	28 days	25
Volatile Organic Compounds	Grab only	G, Teflon-Faced silicone cap	Cool, 4°C HCL to pH<2	14 days	2 x 40

Source: "Characterization of Hazardous Waste Sites," A Method Manual EPA-600/4-84-076.

^aP = Polyethylene, G = Glass

^bThe holding times are those listed in Technical Additions to Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-005 and Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057.

TABLE 14.2
SUMMARY OF ORGANIC SAMPLE CONTAINERS

WATER SAMPLE	REQUIRED VOL.	CONTAINER TYPE
ORGANIC ANALYSIS	1 GALLON	1 x 4-LITER AMBER GLASS BOTTLES OR 2 X 80-OZ. AMBER GLASS BOTTLES OR 4 X 1-LITER AMBER GLASS BOTTLES

TABLE 14.3
SUMMARY OF INORGANIC SAMPLE CONTAINERS

WATER SAMPLE	REQUIRED VOL.	CONTAINER TYPE	PRESERVATION	HOLDING TIME
INORGANIC ANALYSIS	1 LITER	1 x 1-LITER GLASS OR POLYETHYLENE BOTTLE OR 2 x 500 ML GLASS OR POLYETHYLENE BOTTLE	HNO ₃ pH <2 (CN sodium hydroxide pH >12)	METALS - 180 DAYS Hg - 28 DAYS CN - 14 DAYS

SOIL/SEDIMENT SAMPLE	REQUIRED VOL.	CONTAINER TYPE	PRESERVATION	HOLDING TIME^(a)
INORGANIC ANALYSIS	8 OZ	1 x 8-OZ WIDE- MOUTH PLASTIC OR GLASS JAR OR 2 x 4-OZ WIDE- MOUTH PLASTIC OR GLASS JARS (AMBER OR POLY FOR TOC)	4°C +/- 2°C	METALS - 180 DAYS Hg - 28 DAYS CN - 14 DAYS TOC - 28 DAYS

Notes:

- a. No technical holding time criteria, however, validator will use aqueous hold time to form professional opinion on data quality.

STANDARD OEPERATING PROCEDURE 23
X-RAY FLUORESENCE ON-SITE MEASUREMENT

FOR INFORMATION ONLY

Revision Level -1-
April 1995

X-Ray Fluorescence On-Site Measurement Standard Operating Procedure 1 of 15

1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to serve as a guide to the start-up, check-out operation, calibration, and routine use of X-Ray Fluorescence (XRF) instruments for on-site measurement (OM) or fixed facility analysis of hazardous or potentially hazardous metals. It is not intended to replace or diminish the use of the specific manufacturer's operating instructions which contain additional information for optimizing instrument performance and for utilizing it for different applications.

The procedures contained in this SOP are general operating procedures which may be changed as required depending on site conditions, equipment limitations, limitations imposed by the Quality Assurance and/or Quality Control procedure or other protocol limitations. In all instances, the procedures finally employed should be documented and included in any or all final reports.

1.1 Principles of Operation

XRF is a non-destructive simultaneous method providing qualitative and quantitative elemental analysis for a variety of sample types with little or no sample preparation. The basis for the method is detection of fluoresced X-rays characteristic of the elements present in a sample following excitation by a radiation source. Primary X-rays from a sealed radioisotope source contained in the XRF instrument are impinged on the sample resulting in emission of fluorescence secondary X-rays characteristic of the elements present in the sample. A microprocessor-based detector provides the spectral resolution and sensitivity to quantitate metals in soil samples in the 10 - 500 mg/kg range depending on the matrix makeup and the analytes of interest.

2. APPLICABILITY

Solid and liquid samples can be analyzed for the elements aluminum (Al) through uranium (U) with proper X-ray source selection and instrument calibration. Typical environmental applications are:

- Heavy metals in soil (in-situ or samples collected from the surface or from bore hole drillings, etc.), sludges and liquids (e.g., lead (Pb) in gasoline).
- Light elements in liquids (e.g., phosphorus (P), sulfur (S), and chlorine (Cl) in organic solutions).
- Heavy metals in industrial waste stream effluents.
- PCB in transformer oil by analysis for chlorine atoms.

- Heavy metal air particulates collected on membrane filters, either from personnel samplers or from high volume samplers.
- Lead in paint

3. SUMMARY

The XRF analyzer employs radioactive isotopes for the production of primary X-rays. Each source emits a specific energy range of primary X-rays that cause a corresponding range of elements in a sample to emit fluorescent X-rays. When more than one source can excite the element of interest, the appropriate source(s) is selected according to its excitation efficiency for the element of interest.

The sample is positioned in front of the source-detector window, and sample measurement is initiated which exposes the sample to primary radiation from the source. Fluorescent and backscattered X-rays from the sample enter through the detector window and are counted in the detector.

4. INTERFERENCES AND POTENTIAL PROBLEMS

The total method error for XRF analysis is defined as the square root of the sum of squares of both instrument precision and user or application related error. Generally, the instrument precision is the least significant source of error in XRF analysis. User or application related error is generally more significant and will vary with each site and method used. The components of the user or application related error are the following.

4.1 Sample Placement

This is a potential source of error because the X-ray signal decreases as the distance from the radioactive source is increased. However, this error is minimized by maintaining the same distance for each sample, therefore operation in stationary mode is recommended.

4.2 Sample Representivity

This can be a major source of error if the sample does not represent the site. Representivity is affected by the soil macro- and micro-heterogeneity. For example, a site contaminated with pieces of slag dumped by a smelting operation will be more heterogenous than a site contaminated by liquid plating waste. This error can be minimized by either mixing a large volume of sample prior to analyzing an aliquot or by analyzing several locations (in-situ) at each sampling point and averaging the results.

4.3 Reference Analysis

Soil chemical and physical matrix effects may be corrected by using Inductively-Coupled Plasma (ICP) or Atomic Absorption (AA) spectroscopy analyzed site-specific soil samples as calibration or calibration check samples. A major source of error can result if the samples analyzed are not representative of the site and/or if the analytical error is large. Additionally, when comparing XRF results with reference analyses results, the efficiency of the sample digestion reference analysis should be considered. Some digestion methods may breakdown different sample matrices more efficiently than others total hydrofluoric (HF) digestion is recommended when fixed laboratory methods are used to compare to OM XRF results.

4.4 Chemical Matrix Effects

Chemical matrix effects (due to the chemical composition of the sample) result from differences in concentrations of interfering elements. These effects appear as either spectral interferences (peak overlaps) or as X-ray absorption/enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, Fe tends to absorb copper (Cu) X-rays, reducing the intensity of Cu measured by the detector, however this effect can be corrected mathematically. Laboratory analysis using ICP or AA is essential if background contaminant levels are unknown. Soils application software accounts for high iron in soil samples, but the user should consult with the manufacture applications chemist or project chemist about possible effects due to background levels of major constituents.

4.5 Physical Matrix Effects

Physical matrix effects (due to sample morphology) are the result of variations in the physical character of the sample. They may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, consider a sample in which the analyte exists in the form of very fine particles within a matrix composed of much coarser material. If two separate aliquots of the sample are prepared in such a way that the matrix particles in one are much larger than in the other, then the relative volume of analyte occupied by the analyte-containing particles will be different in each. When measured, a larger amount of the analyte will be exposed to the source X-rays in the sample containing finer matrix particles; this results in a higher intensity reading for that sample, and consequently, an apparently higher measured concentration for that element. Sample preparation (Section 8.3) can be designed to minimize error introduced by sample morphology.

4.6 Application Error

XRF instruments have the ability to operate in different modes or applications. Generally, the error in the application calibration is insignificant (relative to the other sources of error) if the instrument's application operating instructions are followed correctly. However, if the sample matrix varies significantly from the design of the application (e.g., using the soils application to analyze a 50% iron mine tailing sample) the application error may become significant.

4.7 Moisture Content

Sample moisture content will affect the analytical accuracy of soils or sludges. The overall error may be a minimal when the moisture range is small (5-20%), or it may be a major source of error when measuring the surface of soils that are saturated with water. Drying samples to a uniform moisture content before analysis is recommended.

4.8 Cases of Severe X-ray Spectrum Overlaps

When present in the sample, certain X-ray lines from different elements can be very close in energy and, therefore, interfere by producing a severely overlapped spectrum. Typical spectral overlaps are caused by the $K\beta$ line of element Z-1 (or as with heavier elements Z-2 or Z-3) overlapping with the $K\alpha$ line of element Z (where Z is the atomic weight). This is the so-called $K\alpha$, $K\beta$ interference. Since the $K\alpha$, $K\beta$ intensity ratio for the given element usually varies from 5:1 to 7:1, the interfering element Z-1 must be present in concentrations greater than Z in order to disturb the measurement, which can often be the case in environmental analyses. The presence of large concentrations of vanadium (Z-1) could disturb the measurement of chromium (Z). The vanadium $K\beta$ energy is 5.427 Kev and the chromium $K\alpha$ energy is 5.41 Kev. The resolution of the detector is not sufficient to separate these energies. Therefore, large amounts of V in a sample will result in spectral overlap with the chromium giving erroneous results.

Other interferences can occur in the overlap of K, L, and M lines of various elements. While these are less common, examples of a severe overlap include arsenic and lead. Unwanted interference can be corrected, however, due to the limits of mathematical corrections, measurement sensitivity is reduced. Generally, As concentrations in samples with Pb:As ratios of 10:1 or more can not be efficiently calculated. This may result in zero As being reported regardless of the actual As concentration.

Identification of the elements present in typical field samples using ICP or similar techniques is essential prior to initiating a field sampling program utilizing XRF.

5. RESPONSIBILITIES

5.1 Project Manager/Project Chemist

The Project Manager or Project Chemist is responsible for ensuring that all Golder Associates personnel engaged in the analysis of soil samples by this procedure have been thoroughly trained in the use of this procedure and the equipment required.

5.2 Project Field Personnel

The project field personnel are responsible for controlling samples in accordance with governing QAPjP, and for complying with the requirements of this procedure.

6. INSTRUMENTATION

6.1 Limits and Precautions

The probe containing the X-ray source should be handled in accordance with the following radiological control practices:

1. The probe should always be in contact with the surface of the material being analyzed and the analyzed material should completely cover the probe opening (aperture) when the sources are exposed. Do not remove a sample or move the probe while the source is in operating mode.
2. When the sources are exposed, under no circumstances should the probe be pointed at the operator or surrounding personnel.
3. Do not place any part of the operator's or co-worker's body in line of exposure when the sources are exposed or partially covered.
4. The probe must be covered with the safety cover or laboratory safety shield when not in use.
5. The appropriate state agency or the Nuclear Regulatory Commission (NRC) office must be notified (see factory supplied data on radiological safety) immediately of any damage to the radioactive source or any loss or theft of the device.
6. Labels or instructions on the probe(s) must not be altered or removed.

7. The user must not attempt to open the probe.
8. The source(s) in the probe must be leak-tested every six months. The leak test certificates must be kept on file and a copy must accompany the instrument at all times.
9. The probe laboratory safety shield assembly must be used when the probe is inverted for measuring samples contained in cups.
10. During operation the probe must be kept at least 10 feet from computer monitors and any other source of radio frequency (RF). Some monitors have very poor RF shielding and will affect measurement results.
11. The instrument should not be dropped or exposed to conditions of excessive shock or vibration.

Additional precautions include:

1. The probe cable must never be pulled while unplugging the probe. The probe plug should be grasped at the ribbed metal connector and squeezed and pulled gently while unplugging the connector. The connector must never be forced when plugging in the connector.
2. The handle of the electronic unit must not be rotated unless the release buttons on each side of the handle are depressed.
3. The instrument should not be stored at an ambient temperature below -4°F or above 110°F.
4. The battery charging unit should only be used indoors in dry conditions.
5. Battery packs should be changed only in dry conditions.

7. REAGENTS

Generally, calibration standards are not necessary for site screening and extent of contamination analyses. Optionally, an application can be optimized or verified to be 1:1 proportional to another analytical (reference) method. This can be done by analyzing a set of Site-Specific Calibration Standards (SSCS) and performing a regression analysis on the reference and the XRF results for each element of concern. In an application any element's calibration can be adjusted by entering the desired slope and offset.

7.1 Site-Specific Calibration Standards (SSCS)

SSCS must be representative of the matrix to be analyzed by XRF. The concentration of the target elements in the SSCS should be determined by independent AA or ICP analyses that meet acceptable quality levels for referee data.

7.1.1 SSCS Sampling

See Section 4.2 on sample representivity. The SSCS samples must be representative of the matrix to be analyzed by XRF. It does not make sense to collect SSCS samples in the site containment area if you are interested in investigating off-site contaminant migration. The matrices may be different and could affect the accuracy of the XRF results. If there are two different matrices on site, collect two sets of SSCS samples.

A full range of target element concentrations is needed to provide a representative calibration curve. Mixing high and low concentration soils to provide a full range of target element concentrations is not recommended due to heterogeneity problems. Unlike liquid samples, solid samples can not be diluted and re-analyzed.

Additionally, collect several SSCS samples in the concentration range of interest. If the action level of the site is 500 mg/kg, providing several SSCS samples bracketing the action level will tend to improve the XRF analytical accuracy in this concentration range.

Generally a minimum of seven appropriate SSCS samples should be taken. A minimum sample size of 4 oz. is recommended. A larger size sample should be taken to compensate for sites with greater content of non-representative material such as rocks and/or organic debris. Standard glass or high-density polyethylene sampling jars should be used.

7.1.2 SSCS Preparation

The SSCS samples should be either air dried overnight or oven dried at less than 105°C. Aluminum drying pans or large plastic weighing boats for air drying may be used. After drying, remove all large organic debris and non-representative material (twigs, leaves, roots, insects, asphalt, rocks, etc.).

The sample should be sieved through a 10-mesh stainless steel sieve. Clumps of soil and sludge should be broken up against the sieve using a stainless steel spoon. Pebbles and organic matter remaining in the sieve should be discarded. The under-sieve fraction of the material constitutes the sample.

Although a maximum final particle size of 10-mesh is normally recommended, a smaller particle size may be desired. The sample should be mixed by dividing the sieved soil into quarters and physically mixing opposite quarters with a clean stainless steel spoon. Re-combine and repeat the quartering and mixing procedure three times. Place the sieved sample in a clean sample jar and label it with both the site name and sample identification information.

The stainless steel sieves should be decontaminated using soap and water and dried between samples.

One or more plastic XRF sample cups should be filled with the sieved soil for each SSCS sample. A piece of 0.2-mil polypropylene film should be cut and stretched until it is wrinkle-free over the top of the X-ray sample cup and then sealed using the plastic securing ring. The cup should be labeled using unique identification information.

Confirmation analyses can be performed on either the XRF sample cup or the balance of the prepared sample. Analysis of the requested element(s) by AA or ICP should be performed on the total hydrofluoric (HF) digest.

8. OPERATIONAL CHECKS

8.1 Blank (Zero) Sample Check

The blank (Zero) sample check is performed to monitor the instrument's zero drift. This should be done once at the beginning of the day after an energy calibration, after loading an application, and whenever the instrument exhibits a persistent drift on a blank or low level sample.

Mount the probe in the laboratory stand and select the appropriate application. Measure the Teflon™ blank provided with the unit using a minimum acquisition time of 60 seconds for each source. Review the results table. Most (95%) of the elemental results should be $0 \pm (2 \times \text{STD})$ (their respective standard deviation), and all of them (99%) should be $0 \pm (3 \times \text{STD})$ (their respective standard deviation). Repeat the measurement if the unit fails to meet these specifications. If several elements continue to be significantly out of these specifications, check the probe window and the blank sample for contamination.

8.2 Target Element Response Check

The purpose of the target element response check is to ensure that the instrument and the selected application are working properly prior to performing sample analysis. This

check should be performed at the beginning of the day. Use low, mid, and high samples or standards with known concentrations for some or all of the target elements to be checked. Select a low sample near the quantitation limit of the target elements. Select a mid sample near the site action level and a high sample near the maximum concentration of the target elements expected on site.

These samples should be measured using the same source acquisition times that will be used for sample analysis. Save the sample check results and spectra for documentation.

8.3 Sample Handling and Preparation

Sample handling and preparation is dependent upon the data use and goals of the investigation. Sample preparation can range from direct in-situ measurements, in which the soil or other surface measurements are made with minimal sample preparation, to sample grinding and/or analysis of sieve fractions without grinding. A maximum particle size of -10 mesh is recommended for prepared samples to achieve uniform particle size between samples, but smaller particles may be desirable in order to characterize transport mechanism (such as wind-borne or surface water transport). Sample preparation techniques should be described in site specific plan documents.

When making XRF measurements, be sure to maintain constant measurement geometry in order to minimize variations in analysis results. Document any anomalies in measurement geometry, sample surface morphology, moisture content, sample grain size, and matrix.

8.4 Soil Samples

Soil samples may be analyzed either in-situ or in prepared X-ray sample cups. Operating the XRF in a soils application assumes the sample to be infinitely thick. For in-situ measurements this is almost always the case but for sample cup measurements it is advisable to fill the cup nearly full and tap it on the bench to compact the soil. This ensures that the sample is as uniformly thick as possible from sample to sample. A safety shield should be used when analyzing sample cups.

Sample where analyses is performed in-situ should first be prepared by removing large rocks and debris from the area in contact with the probe. The soil surface should be rendered flat and compact prior to analysis. The XRF probe should be held firmly on the ground to maximize instrument contact with the ground. The probe should not be moved during analysis. Analysis of water saturated soils should be avoided. A thin layer of 0.2-mil polypropylene XRF film may be mounted on the surface probe to minimize contamination. Use of varying thicknesses of plastic (bags) have been shown to interfere

with light element measurements and may affect the calibration of other elements. Additionally, plastic may contain significant levels of target element contamination.

Course-grained soils conditions, nuggets of contaminated material, or rock may not permit a truly representative sample and may adversely bias the analytical result. Such samples should be prepared before analysis. Preparation consistency is important to minimize variation in analytical results. Crushing the sample which has been folded into a cotton rag with a small sledge hammer has proven to be effective field sample preparation method.

9. ROUTINE FIELD PROCEDURES

9.1 Calibration

Standardless

FPXRF can be equipped with fundamental parameter capabilities which allow for standardless calibration. It uses calibration curves based on matrices similar to those of the routine samples.

Site Typical

A site typical calibration curve is based on samples similar in composition, but not necessarily matrix matched. Extreme caution should be exercised when using a site-typical calibration curve. Situations have been encountered where increased iron levels in mine tailings relative to the calibration standards resulted in anomalously high chromium results (in excess of several wt% Cr!). Corroboratory analyses found chromium in the zero to 40 mg/kg range.

Site Specific

To minimize enhancement/absorption and spectral interference errors, calibration standards should be collected from the specific site in question. These Site Specific Calibration (SSC) standards must closely emulate the physical and chemical matrix of the routine samples. The SSC standards are prepared identically to field samples so that the particle size bias of the routine samples is included in the instrument calibration.

Characterization of the SSC standard must be done using a total digestion procedure rather than a partial extraction because XRF is a total analyte method independent of phase or specification.

10. QUALITY ASSURANCE/QUALITY CONTROL

10.1 Precision

The precision of the method is monitored by reading the low or mid SSCS at the start and end of sample analysis and after approximately every tenth sample (a daily total of seven measurements is recommended). Determining the precision around the site action level can be extremely important if the XRF results are to be used in an enforcement action. Therefore, selection of an SSCS at or near the site action level or level of concern is recommended. The sample is analyzed by the instrument for the normal field analysis time and the results are recorded. The standard deviation for each dependent element is calculated. The relative standard deviation (RSD) of the sample mean can be used to calculate precision. The RSD should be within $\pm 40\%$ for the data to be considered adequately precise.

10.1.1 Preliminary Detection Limit (DL) and Quantitation Limit (QL)

A preliminary DL and QL is needed to give the operator an indication of the instrument's capability out in the field. A low or blank SSCS sample is selected as described in Section 7.1. More than one standard may be needed to obtain low or blank concentration values for each element. Alternatively, the Teflon blank may be used if a blank soil or sediment sample is unavailable.

The sample is measured ten times without moving it using the anticipated field analysis measuring time. The standard deviation of the mean for each target element is calculated (using the N-1 formula).

If the standard deviation has a fractional component round up to the next whole number prior to calculating the DL and QL.

The definition of the DL is three times the calculated standard deviation value.

The definition of the QL is 10 times the calculated standard deviation value.

10.1.2 The Method Minimum Detection Limit (MMDL) and Method Quantitation Limit (MQL)

The MMDL and MQL are calculated from the measurement of a low SSCS selected as described in Section 7.1 at the start and end of sample analysis and after approximately every tenth sample (a daily total of seven measurements is recommended).

Disable the display thresholds. This will permit results less than one standard deviation (STD) to be displayed (even negatives). Measure the SSCS using the same analysis, measuring time used for the samples. Enable the display thresholds prior to analyzing the next sample.

The standard deviation of the mean for each target element is calculated. If the standard deviation has a fractional component round up to the next whole number prior to calculating the MMDL and MQL.

The definition of the MMDL is three times the calculated standard deviation value.

The definition of the MQL is 10 times the calculated standard deviation value.

10.2 Reporting Results

All raw XRF data should be reported including the individual results of multiple analyses of samples and sampling points. The average and concentration range of each multiple analysis should also be reported.

A "reported" value for each analysis or average of multiple analyses should be processed in the following manner.

1. Round the value to the same degree of significance contained in the SSCS sample assay values (usually two) if the element's calibration has been adjusted (see Section 6.0).
2. Report all values less than or equal to the MMDL as not detected (ND).
3. Flag and note all values greater than the MMDL and less than or equal to the MQL as estimated (usually with a "J" next to the reported value).
4. Report all values above the MQL and within the linear calibration range (if the element's calibration has been adjusted (see Section 6.0).
5. Flag and note all values above the linear calibration range (greater than the highest SSCS used in the calibration adjustment procedure) with a "*" next to the reported value.

10.3 Accuracy

Accuracy, relative to a specific digestion method and elemental analysis procedure is determined by confirmation of the XRF sample result (prepared sample cups may be submitted) with AA or ICP analysis.

To do a total accuracy check, confirmation samples should be collected throughout the entire sampling effort. A minimum of 10% of the samples should be collected including a number of samples at or near the action level. The results of the metal analysis (dependent) and the XRF analysis (independent) are evaluated with a regression analysis. The correlation coefficient (r^2) should be 0.7 or greater. All XRF results should be presented along with an estimate of the error based on confirmation analyses.

Another very important source of potential difference between XRF and AA or ICP results is incomplete digestion employed prior to ICP or AA analyses. Since XRF is a total elemental technique, any comparison with referee results must account for the possibility of variable extraction depending upon the extraction method used and its ability to dissolve the mineral form in question.

10.3.1 Matrix Considerations

Other types of QA/QC verification should include verification that the instrument calibration is appropriate for the specific site to be assessed. This includes verification of potential multiple soil matrix types that may exist at a site. Matrix variations that affect the XRF measurement include large variations in calcium content such as may be encountered when going from siliceous to calcareous soils as well as variations in iron content.

11. DATA VALIDATION

11.1 Confirmation Samples

Confirmation samples are recommended at a minimum rate of 10%. Ideally, the sample cup that was analyzed by XRF should be the same sample that is submitted for AA/ICP analysis. When confirming an in-situ analysis, collect a sample from a 6 inch by 6 inch area for both an XRF measurement and confirmation analysis. The correlation coefficient between XRF and AA/ICP data should be 0.7 or greater.

11.2 Recording Results

Record all results and monitoring activities in a laboratory or field notebook. Alternatively, record results electronically on a hard drive or floppy disk.

12. HEALTH AND SAFETY

When working with potentially hazardous materials follow USEPA, OSHA, GAI and/or any other applicable health and safety practices.

13. REFERENCES

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8. Chappell, R., Davis, A., Olsen, R. "Portable X-ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes." Proceedings Conference Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., 1986, p. 115.

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13. SPECTRACE 9000 "Field-Portable X-Ray Fluorescence." U.S EPA/ERT Standard Operating Procedures (SOP) Number 1713, Rev. 0.0, August 31, 1992.

SOP 23a – Procedures for Metals Analysis Using Field Portable X-Ray Fluorescence Analyzers

I. Scope and Application

This SOP provides general guidance for the operation of XRF instruments for the analysis of inorganic metals in soil. The SOP describes general principles, materials and methodology used for intrusive XRF and technical information from the manufacturer for the specific equipment that will be employed. Attached to this SOP is the USEPA SW-846 Method 6200 Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment, which will be utilized where appropriate.

XRF analyses will be conducted on the homogenized soil samples. As described in USEPA Method 6200, additional enhancements to the sample preparation (i.e., drying, grinding) may also be required to achieve lower detection limits and/or to decrease soil heterogeneity. Procedures will be adjusted, as necessary, to accommodate additional sample preparation.

II. Materials

The following materials, as required, will be available during XRF soils analysis:

- Personal protective equipment (as required by the Health and Safety Plan (HASP) [BBL, 2005]);
- Cleaning and decontamination equipment (as specified in Attachment C);
- Analyzer unit with data acquisition, processing, display, and computer interface;
- Computer and printer;
- Testing stand;
- Lithium-ion batteries;
- Battery charging system;
- Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (as specified for the XRF instrument);
- X-ray window film: Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent 2.5 to 6.0 micrometers (μm) thick;
- Moisture content meter (e.g., AEMC CA847);
- Mortar and pestle;
- Pure element standards (e.g., Pb);
- Equipment blank samples (e.g., pure silica dioxide);
- Method blank samples [e.g., pure silica sand];
- Calibration standard (e.g., standard reference material);
- Drying oven (convection or toaster oven);
- Thermometer;
- Aluminum or stainless steel bowl and tray;
- Appropriate containers, labels, and forms;
- Field notebook;
- Camera and film (or digital camera);
- Field equipment logbook;
- Property analysis results notebook; and
- Instrument operation manual.

III. Procedures

The following procedures will be used to perform the XRF analysis:

Sample Preparation

1. Don personal protective equipment (as required by the HASP).
2. Empty soil contents from sampling jar into labeled sample tray and record sample information within field notebook.
3. Remove any debris (e.g., twigs, rocks, etc.) from sample.
4. Measure moisture content using a moisture content meter (e.g., AEMC CA847), and record in field notebook. If moisture content is greater than twenty percent (20%), then place sample tray in oven for 2 to 4 hours at a temperature of less than 150°C. Oven temperature will be recorded once per day using thermometer. If not, then proceed to sample analysis.
5. If necessary due to soil characteristics (e.g., coarseness), grind sample using mortar and pestle.
6. Place approximately 5 gm of the sample contents into polyethylene sample cups and cover tightly with x-ray window film.
7. Place sample cup under x-ray window according to manufacturer's instructions.
8. Clean sample preparation equipment in accordance with the procedures in FSP.

Quality Assurance/Quality Control

1. Follow QA/QC procedures as specified in QAPP and in accordance with manufacturer instructions and USEPA Method 6200.
2. Perform energy calibration check sample at least twice daily. This test is typically done automatically within the equipment during the startup or standardization procedures using a pure element standard (e.g., Pb, Fe, Cu). Appropriate energy calibration information (e.g., date, time, etc.) will be recorded within the field equipment logbook.
3. Analyze equipment blank at a specified frequency (e.g., 1 per 20 samples) using pure silicon dioxide. Record date, time, and result within the field equipment logbook.
4. Analyze method blank at a specified frequency (e.g., 1 per 20 samples) using clean silica sand which will undergo the same sample preparation procedures as a field sample to ensure that there is no cross-contamination during the sample preparation procedure. Record date, time, and result within the field equipment logbook.
5. Analysis of calibration verification check (CVC) sample will be performed so that the CVC will bracket sample analysis at a specified frequency (e.g., once prior to analysis and at the end of the analysis batch at frequency of no less than 1 per 20 samples) using standard reference materials (SRMs) at concentrations approximately at the RALs and/or at the detection limits from an outside vendor. The

measured value for each target analyte should be within $\pm 20\%$ difference of the true value for the calibration verification check to be acceptable. If any measured value falls outside this range, then the check sample should be reanalyzed. If the values continue to fall outside the acceptable range, the instrument should be recalibrated and the previous batch of samples analyzed before the unacceptable calibration verification must be reanalyzed.

6. Analyze precision measurement [e.g., test relative standard deviation (RSD) amongst 7 replicates] at a specified frequency (e.g., once per day) using field samples. The selected field samples (when possible) will exhibit XRF-targeted metals concentration ranges between approximately $1/5^{\text{th}}$ the RAL and approximately the RAL. If the RSD value exceeds twenty percent (20%) [30% for Cr], then an increase in sample count time is necessary. The sample count time will increase by 30-second increments until an acceptable RSD is achieved. Record date, time, and result within the field equipment logbook.
7. Average site-specific method detection limits (MDL) and practical quantitation limits (PQLs) will be generated using results from replicate (7) analyses of the low concentration SRM samples. The method detection limit will be defined as 3 times the standard deviation of the results and the method quantitation limit will be defined as 10 times the standard deviation of the same results.
8. Confirmatory samples to determine comparability of the XRF analysis to laboratory results will follow procedures outlined in the Work Plan and Section 8.1 of the QAPP Addendum (Attachment 4 of the Work Plan).

Calibration and Standardization

1. Instrument calibration processes may incorporate any one of three types of procedures existing for XRF instruments: Fundamental Parameters (FP) calibration, empirical calibration, and the Compton peak ratio or normalization method. The calibration procedure will be dependent upon the XRF instrument and data quality objectives specified.

Sample Analysis

1. Don personal protective equipment (as required by the HASP).
2. Start up analyzer equipment (as per manufacturer's instructions) and allow 15 minutes for warm up.
3. Check battery life. If low, then replace before proceeding.
4. Set up instrument for soil testing for target analytes (as per manufacturer instructions). This will include entering target analytes, associated action limits, sample time, and sample identification number.
5. Remove an aliquot of the soil from the sample jar and follow sample preparation procedure above.
6. Run soil sample according to specified target analytes and associated data quality objectives (e.g., RALs). Based on the potential interference amongst certain analytes (e.g., Pb and As), sample times will be determined based on the effectiveness of the XRF equipment and the level of resolution desired.
7. Once the desired resolution has been met for the target analytes, end sampling run.
8. Remove sample cup from analyzer and return soil sample to the sample container.

Data and Reporting Procedures

1. Upon completion of sample analysis, export all readings and spectrum data for the day to connected portable computer.
2. Save data files according to project database requirements.
3. Using Microsoft® Access, import electronic data files into the project database using the utilities (e.g., EDD Import Form) provided in the common repository for environmental data (CORE) database structure.
4. Using the “generate tables” form within CORE, select appropriate parameters (e.g., specific properties, sample IDs, analytes, etc.) and output data summary table to Microsoft® Excel. All electronic data (e.g., database) will be uploaded to the project BBL website at the end of the work shift and automatically backed up by the server.
5. Print out a hardcopy for results notebook. Follow appropriate project requirements for any additional data deliverables (e.g., hardcopies for agencies and property owners, e-mail to project manager, etc.).

Standard Operating Procedure: Sediment Core Collection

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures to collect sediment core samples.

II. Personnel Qualifications

To be completed by Preparer and reviewed by Technical Expert.

III. Equipment List

Sediment Sampling Equipment

The following materials will be needed during sediment sampling activities:

- aluminum boat with outboard motor;
- health and safety equipment, as required by the site Health and Safety Plan (HASP);
- cleaning equipment;
- aluminum or stainless steel tray;
- duct tape;
- Lexan tubing with end caps;
- brass push rod;
- hacksaw;
- stainless steel core driver;
- vacuum pump;
- piston sampler;
- photoionization detector (PID);
- 6-foot rule or survey rod;
- transport container with ice;
- appropriate sample containers and forms; and
- field notebook.

Field Cleaning Equipment

The following equipment will be needed for field cleaning after sediment sampling is completed:

- health and safety equipment (as required in the HASP);
- distilled water (laboratory-supplied);
- non-phosphate soap (Alconox or equivalent);
- distilled water;
- appropriate cleaning solvent (e.g., hexane);
- rinse collection plastic containers;

- brushes;
- aluminum foil;
- garbage bags;
- spray bottles for solvent; and
- Ziploc-type bags.

IV. Cautions

To be completed by Preparer and reviewed by Technical Expert.

V. Health and Safety Considerations

To be completed by Preparer and reviewed by Technical Expert.

VI. Procedure

Sediment Sampling Procedure

1. Identify the proposed sample location in the field notebook along with other appropriate information collected during the sediment probing activities.
2. Don personal protective equipment (PPE), as required by the HASP.
3. At each sample location, lower a section of Lexan tube until it just reaches the top of sediment. Measure the depth of water. (Sections of Lexan tube may need to be spliced together in deep water locations.)
4. Push the Lexan tube into the sediment by hand until refusal. Measure the depth of sediment.
5. Drive the tube several more inches using a stainless steel core driver block and measure the distance. This procedure is performed to obtain a “plug” at the bottom of the core and prevent the loose sediment from escaping;
6. Pump the water out from inside the Lexan tubing.
7. Place a vacuum pump on the top end of the Lexan tube and create a vacuum to prevent the sediments/plug from escaping.
8. Slowly pull the tube from the sediment, twisting it slightly as it is removed (if necessary).
9. Before the tube is fully removed from the water, place a cap on the bottom end of the tube while it is still submerged.
10. Keeping the tube upright, wipe the bottom end dry and seal the cap with duct tape and label. Measure the length of sediment recovered and evaluate the integrity of the core. If the core is not suitably intact, repeat coring procedure within 5 to 10 feet of the first location attempted.

11. While still keeping the core upright, use a hacksaw to make a horizontal cut in the tube approximately 1 inch above the sediment.
12. Re-cap the cut end of the tube, seal the cap with duct tape, and mark this end as “top.”
13. Wipe the tube dry.
14. Place a completed sample label on the tube.
15. Record the following information on both the tube and on the cap: 1) sample number; 2) sampling date; and 3) sampling time.
16. Place the core sample upright in a container with ice.
17. Repeat the above procedures until the appropriate number of core samples are collected (for the sampling event or the sampling day).
18. Extrude the sediment cores from the Lexan tubing onto an aluminum or stainless steel tray. Describe and record sample description, including depths at which sediment characteristics change and visual characteristics.
19. Section the sediment cores into the intervals determined for the project. Use a decontaminated hacksaw or knife to section the sediment cores. Characterize each sediment sample for color, texture, and visual staining/odors. Place each sediment sample into the appropriate laboratory-supplied sample containers.
20. Label all sample containers according to the appropriate procedures.
21. Handle, pack, and ship samples using the chain-of-custody procedures in accordance with the appropriate SOP.

Field Cleaning Procedure

1. Follow health and safety procedures specified in the HASP.
2. Cleaning of reusable sampling equipment (e.g., trays, spatulas, scoops, and core driver) will follow the decontamination procedures presented in the equipment cleaning SOP.
3. Cleaning will be conducted in plastic containers to collect all decontamination rinsate.

VII. Waste Management

Materials generated during the sediment sampling activities and disposable equipment will be transported for offsite disposal in accordance with applicable rules and regulations.

VIII. Data Recording and Management

To be completed by Preparer and reviewed by Technical Expert.

IX. Quality Assurance

To be completed by Preparer and reviewed by Technical Expert.

X. References

To be completed by Preparer and reviewed by Technical Expert.

XI. References

To be completed by Preparer and reviewed by Technical Expert.

Appendix D

NPDES Forms



Notice of Intent (NOI) for Storm Water Discharges Associated with Construction Activity Under an NPDES General Permit

I. Permit Number

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[illegible]

IRS Employer Identification Number (EIN): -

Street:

City: | | | | | State: | Zip Code: | - |

Phone: | | | - | | | - | | | | Fax (optional): | | | - | | | - | | | |

[illegible][illegible][illegible]

City: State: Zip Code: -

[illegible]

Latitude

1. ___° ___' ___" N (degrees, minutes, seconds)
2. ___° ___' . ___' N (degrees, minutes, decimal)
3. ___ . ___° N (decimal)

Longitude 1. ____° ____' ____" W (degrees, minutes, seconds)
2. ____° ____' ____" W (degrees, minutes, decimal)
3. ____° W (decimal)

Method: U.S.G.S. topographic map EPA web site GPS Other: _____

• If you used a U.S.G.S. topographic map, what was the scale: _____

Project Located in Indian country?	Yes	No
If so, name of Reservation or if not part of a Reservation, put "Not Applicable":		

Estimated Project Start Date: / / Estimated Project Completion Date: / /
 Month Date Year Month Date Year

Estimated Area to be Disturbed (to the nearest quarter acre):

IV. SWPPP Information

Has the SWPPP been prepared in advance of filing this NOI? Yes No

Location of SWPPP for viewing: Address in Section II Address in Section III Other

If Other:

SWPPP Street:

City:

State: Zip Code: -

SWPPP Contact Information (if different than that in Section II):

Name:

Phone: - - Fax (optional): - -

E-mail (optional):

V. Discharge Information

Identify the name(s) of waterbodies to which you discharge.

Is this discharge consistent with the assumptions and requirements of applicable EPA approved or established TMDL(s)?

Yes No

VI. Endangered Species Information

Under which criterion of the permit have you satisfied your ESA eligibility obligations?

A B C D E F

- If you select criterion F, provide permit tracking number of operator under which you are certifying eligibility:

VII. Certification Information

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Print Name:

Print Title:

Signature:

Date:

**Notice of Intent (NOI) for Storm Water Discharges Associated with
Construction Activity Under an NPDES General Permit**

NPDES Form

This Form Replaces Form 3510-9 (8/98)

Form Approved OMB Nos. 2040-0188 and 2040-0211

Who Must File an NOI Form

Under the provisions of the Clean Water Act, as amended (33 U.S.C. 1251 et seq.; the Act), federal law prohibits storm water discharges from certain construction activities to waters of the U.S. unless that discharge is covered under a National Pollutant Discharge Elimination System (NPDES) Permit. Operator(s) of construction sites where one or more acres are disturbed, smaller sites that are part of a larger common plan of development or sale where there is a cumulative disturbance of at least one acre, or any other site specifically designated by the Director, must submit an NOI to obtain coverage under an NPDES general permit. Each person, firm, public organization, or any other entity that meets either of the following criteria must file this form: (1) they have operational control over construction plans and specifications, including the ability to make modifications to those plans and specifications; or (2) they have day-to-day operational control of those activities at the project necessary to ensure compliance with SWPPP requirements or other permit conditions. If you have questions about whether you need an NPDES storm water permit, or if you need information to determine whether EPA or your state agency is the permitting authority, refer to www.epa.gov/npdes/stormwater/cgp or telephone the Storm Water Notice Processing Center at (866) 352-7755.

Where to File NOI Form

See the applicable CGP for information on where to send your completed NOI form.

Completing the Form

Obtain and read a copy of the appropriate EPA Storm Water Construction General Permit for your area. To complete this form, type or print, using uppercase letters, in the appropriate areas only. Please place each character between the marks (abbreviate if necessary to stay within the number of characters allowed for each item). Use one space for breaks between words, but not for punctuation marks unless they are needed to clarify your response. If you have any questions on this form, refer to www.epa.gov/npdes/stormwater/cgp or telephone the Storm Water Notice Processing Center at (866) 352-7755. Please submit original document with signature in ink - do not send a photocopied signature.

Section I. Permit Number

Provide the number of the permit under which you are applying for coverage (see Appendix B of the general permit for the list of eligible permit numbers).

Section II. Operator Information

Provide the legal name of the person, firm, public organization, or any other entity that operates the project described in this

application. An operator of a project is a legal entity that controls at least a portion of site operations and is not necessarily the site manager. Provide the employer identification number (EIN from the Internal Revenue Service; IRS), also commonly referred to as your taxpayer ID. If the applicant does not have an EIN enter "NA" in the space provided. Also provide the operator's mailing address, telephone number, fax number (optional) and e-mail address (if you would like to be notified via e-mail of NOI approval when available). Correspondence for the NOI will be sent to this address.

Section III. Project/Site Information

Enter the official or legal name and complete street address, including city, state, zip code, and county or similar government subdivision of the project or site. If the project or site lacks a street address, indicate the general location of the site (e.g., Intersection of State Highways 61 and 34). Complete site information must be provided for permit coverage to be granted.

The applicant must also provide the latitude and longitude of the facility either in degrees, minutes, seconds; degrees, minutes, decimal; or decimal format. The latitude and longitude of your facility can be determined in several different ways, including through the use of global positioning system (GPS) receivers, U.S. Geological Survey (U.S.G.S.) topographic or quadrangle maps, and EPA's web-based siting tools, among others. Refer to www.epa.gov/npdes/stormwater/cgp for further guidance on the use of these methodologies. For consistency, EPA requests that measurements be taken from the approximate center of the construction site. Applicants must specify which method they used to determine latitude and longitude. If a U.S.G.S. topographic map is used, applicants are required to specify the scale of the map used.

Indicate whether the project is in Indian country, and if so, provide the name of the Reservation. If the project is in Indian Country Lands that are not part of a Reservation, indicate "not applicable" in the space provided.

Enter the estimated construction start and completion dates using four digits for the year (i.e., 05/27/1998). Enter the estimated area to be disturbed including but not limited to: grubbing, excavation, grading, and utilities and infrastructure installation. Indicate to the nearest quarter acre. Note: 1 acre = 43,560 sq. ft.

Section IV. SWPPP Information

Indicate whether or not the SWPPP was prepared in advance of filing the NOI form. Check the appropriate box for the location where the SWPPP may be viewed. Provide the name,

**Notice of Intent (NOI) for Storm Water Discharges Associated with
Construction Activity Under an NPDES General Permit**

NPDES Form

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Form Approved OMB Nos. 2040-0188 and 2040-0211

fax number (optional), and e-mail address (optional) of the contact person if different than that listed in Section II of the NOI form.

Section V. Discharge Information

Enter the name(s) of receiving waterbodies to which the project's storm water will discharge. These should be the first bodies of water that the discharge will reach. (Note: If you discharge to more than one waterbody, please indicate all such waters in the space provided and attach a separate sheet if necessary.) For example, if the discharge leaves your site and travels through a roadside swale or a storm sewer and then enters a stream that flows to a river, the stream would be the receiving waterbody. Waters of the U.S. include lakes, streams, creeks, rivers, wetlands, impoundments, estuaries, bays, oceans, and other surface bodies of water within the confines of the U.S. and U.S. coastal waters. Waters of the U.S. do not include man-made structures created solely for the purpose of wastewater treatment. U.S. Geological Survey topographical maps may be used to make this determination. If the map does not provide a name, use a format such as "unnamed tributary to Cross Creek". If you discharge into a municipal separate storm sewer system (MS4), you must identify the waterbody into which that portion of the storm sewer discharges. That information should be readily available from the operator of the MS4.

Indicate whether your storm water discharges from construction activities will be consistent with the assumptions and requirements of applicable EPA approved or established TMDL(s). To answer this question, refer to www.epa.gov/npdes/stormwater/cgp for state- and regional-specific TMDL information related to the construction general permit. You may also have to contact your EPA regional office or state agency. If there are no applicable TMDLs or no related requirements, please check the "yes" box in the NOI form.

Section VI. Endangered Species Information

Indicate for which criterion (i.e., A, B, C, D, E, or F) of the permit the applicant is eligible with regard to protection of federally listed endangered and threatened species, and designated critical habitat. See Part 1.3.C.6 and Appendix C of the permit. If you select criterion F, provide the permit tracking number of the operator under which you are certifying eligibility. The permit tracking number is the number assigned to the operator by the Storm Water Notice Processing Center after EPA acceptance of a complete NOI.

Section VII. Certification Information

All applications, including NOIs, must be signed as follows:

For a corporation: By a responsible corporate officer. For the purpose of this Section, a responsible corporate officer means:

(i) a president, secretary, treasurer, or vice-president of the corporation in charge of a principal business function, or any other person who performs similar policy- or decision-making functions for the corporation, or (ii) the manager of one or more manufacturing, production, or operating facilities, provided, the manager is authorized to make management decisions which govern the operation of the regulated facility including having the explicit or implicit duty of making major capital investment recommendations, and initiating and directing other comprehensive measures to assure long-term environmental compliance with environmental laws and regulations; the manager can ensure that the necessary systems are established or actions taken to gather complete and accurate information for permit application requirements; and where authority to sign documents has been assigned or delegated to the manager in accordance with corporate procedures.

For a partnership or sole proprietorship: By a general partner or the proprietor, respectively; or

For a municipality, state, federal, or other public agency: By either a principal executive officer or ranking elected official. For purposes of this Part, a principal executive officer of a federal agency includes (i) the chief executive officer of the agency, or (ii) a senior executive officer having responsibility for the overall operations of a principal geographic unit of the agency (e.g., Regional Administrator of EPA).

Include the name and title of the person signing the form and the date of signing. An unsigned or undated NOI form will not be considered eligible for permit coverage.

Paperwork Reduction Act Notice

Public reporting burden for this application is estimated to average 3.7 hours. This estimate includes time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. An agency may not conduct or sponsor, and a person is not required to respond to, a collection of information unless it displays a currently valid OMB control number. Send comments regarding the burden estimate, any other aspect of the collection of information, or suggestions for improving this form, including any suggestions which may increase or reduce this burden to: Chief, Information Policy Branch 2136, U.S. Environmental Protection, Agency, 1200 Pennsylvania Avenue, NW, Washington, D.C. 20460. Include the OMB control number on any correspondence. Do not send the completed form to this address.